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Molecular catalysts for hydrogen production from alcohols

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Abstract

An industrially applicable catalytic methodology for dihydrogen formation from a proton source remains at the forefront of all efforts to replace the present fossil fuel economy by a hydrogen economy. This review tries to summarize the achievements which have been made with molecular organometallic complexes as catalysts for the dehydrogenation of alcohols. Biology uses NAD^+ as metal-free hydrogen acceptor which converts with the help of enzymes (alcohol dehydrogenase, aldehyde dehydrogenase) alcohols in carbonyl compounds, NADH, and protons. In the regeneration of NADH to NAD^+, electrons are stored in electron transfer enzymes (ferredoxines) which are subsequently used to reduce protons to hydrogen with the help of hydrogenases or nitrogenases which ensure a very low overpotential for the reduction. Man-made organometallic complexes are rather primitive with respect to this complex machinery but use some principles from biology as guide line. Classical complexes like rhodium or ruthenium phosphane complexes achieve at best a few thousands of turn over frequencies (TOFs). Established reactions like oxidative addition of the hydroxyl group of the substrate to the metal centre, β-hydrogen elimination from the α-CH group of the coordinated alcohol, product dissociation, and reductive elimination of hydrogen are involved in the proposed catalytic cycles. Complexes which show metal-ligand cooperativity show a significantly better performance with respect to turn over frequencies (conversion rate = activity) and turn over numbers (number of product molecules per catalyst molecule = efficiency). In these catalytic systems, the alcohol substrate is converted with the help of active centres in the ligand backbone which participate directly and reversibly in the transformation of the substrate. Present results indicate that dehydrogenative coupling reactions of the type, $R\text{-}CH_2\text{-}OH + XH \rightarrow RCOX + 2\ H_2$ proceed especially well and can be applied to a wide range of substrates including multiple dehydrogenative couplings leading to polyester or polyamides. In photocatalytic conversions, alcohols can be deoxygenated to hydrocarbons, CO, and H_2 which should be further explored in the future. New developments consist in the construction of organometallic fuel cells (OMFCs) where the anode is composed out of molecular catalyst embedded into a conducting support material. Here no free hydrogen is evolved but is directly converted to electric current and protons according to $H_2 \rightarrow 2H^+ + 2\ e$. The review

focuses on the catalysis with organometallic complexes but lists some selected results obtained with heterogeneous catalytic systems for comparison.

1. Introduction

"What will replace cheap oil...and when?"
In the top of the 25 questions of "what we do not know?" Science 125th anniversary.[1]

Industry generates more than 50 million metric tons of hydrogen each year from fossil fuels.[2] While half of the production is dedicated to the synthesis of NH_3 by the Haber-Bosch process, the second part is mainly consumed by oil refineries. In the future, the demand for hydrogen may increase significantly by operating fuel cell systems.[3] Hydrogen is an ideal energy carrier that is easily converted to electricity using fuel cell technology, liberates a large amount of energy per unit mass, and does not generate pollutants. While unquestionably energy efficient water splitting into oxygen and hydrogen is the method of choice for large scale H_2 production, the past years have witnessed substantial improvements in the production of hydrogen from stable hydrogen-rich molecules with the help of new catalysts. Alcohols can be considered as "organic" molecular storage forms of energy. The utilization of this type of compounds may solve problems related with storage and transport of large quantities of hydrogen to potential users worldwide using the existing infrastructure. The efficient catalyzed decomposition of alcohols into molecular hydrogen and oxidized compounds, which may be of value themselves, offers the possibility of using stable and easily storable compounds as a source of hydrogen for fuel cells. Figure 1 shows the development of the number of publications over the last two decades which are obtained when the terms "alcohols" and "fuel cells" are linked in a literature search.[4a] Most of the publications stem from US research institutions. Likely, the steep increase in publishing activity at the beginning of the new millennium is due to an initiative in the USA which focused on hydrogen as a fuel around 2002 and 2003.[4b] About five years later, a plateau phase is reached with a steady number of about 350 papers per year publications which may reflect the enormous challenges and difficulties in achieving a real breakthrough which would again initiate intense research activities.

This review will focus on the progress which was achieved in the hydrogen production from alcohols with molecular catalysts in homogeneous phase. Very brief comparisons to some heterogeneous systems will be made and some principles of catalysts operating in biological systems will also be addressed.

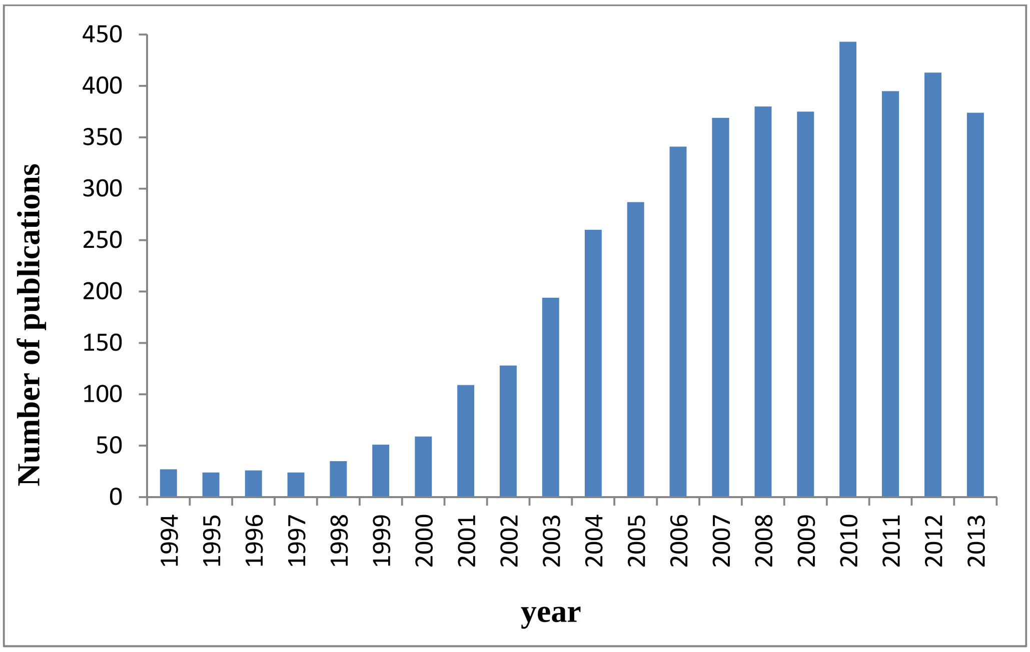


Figure 1. Number of publications in the past 2 decades obtained with the search terms “alcohol and fuel cell”[4a]

Different alcohol substrates from the simplest like methanol or ethanol to polyols (glycerol, sugars) derived from biomass can be considered as resource for the production of H_2. The energy required to generate hydrogen from the fuel substrate will be compensated by the exothermic reaction between H_2 and O_2 which amounts to $\Delta H°_R = -242$ kJ mol^{-1} per equivalent of H_2. The role of the catalyst is to minimize the activation barriers for the individual steps involved in the dehydrogenation. Hence, the goal is to find an alcoholic fuel with a high hydrogen content which can be converted with a minimum of energy investment into a dehydrogenated (oxidized) product and hydrogen. In Table 1 we summarize the thermodynamic data for several dehydrogenative conversions of methanol, ethanol, and a secondary alcohol like 2-propanol to aldehydes, carbon monoxide or acetone. Furthermore, we list the data for selected dehydrogenative coupling reactions in which primary alcohols react with water, a second equivalent of an alcohol, or ammonia to the corresponding carboxylic acid derivatives (i.e. acids, esters, or amides) with concomitant formation of molecular hydrogen. For every fuel, the potential “fuel energy”, ΔE_F, which can be gained in the overall process through the combustion of H_2 with O_2 is given as $\Delta E_F = [n\ \Delta H_R(H_2 + ½O_2) - \Delta H_r]$ with n = number of equivalents of H_2 liberated in the dehydrogenation step.

Methanol is the least expensive alcohol on the current market and does not interfere directly with the food chain. Although nowadays it is produced mainly from syn-gas, which is obtained by catalytic reforming of fossil fuel, it can also be obtained through the hydrogenation of CO_2. Olah *et al.* suggested in late 90s an economy based on methanol. Methanol is a promising fuel, since it is stable, liquid under ambient conditions, and has a high content of hydrogen.[5] The development of efficient processes for releasing hydrogen from methanol or for the direct conversion in electrical energy (in direct methanol fuel cells, DMFC) is essential for the success of this proposition. New strategies for steam reforming of methanol under mild conditions based on heterogeneous or molecular catalysts have raised the hopes and expectations in this fuel. As entries 1 and 2 (Table 1) show, the sequential conversion of methanol to formaldehyde and formaldehyde to carbon monoxide requires in total 89.1 kJ mol^{-1} + 5.4 kJ mol^{-1} = 94.5 kJ mol^{-1}, which is compensated by combustion of the weight content of about 12.5 wt% H_2 which makes the overall reaction sequence, $H_3COH \rightarrow CO + 2\ H_2$ and $2\ H_2 + O_2 \rightarrow 2\ H_2O$, exothermic by $\Delta E_F = -389.5$ kJ mol^{-1}. However, the formation of CO is a principal problem when a homogeneously catalyzed process is envisioned, because catalyst deactivation may occur. The equations shown in entries 3 to 6 show a possible solution to this problem. Instead of dehydrogenating formaldehyde ($H_2C{=}O$) to CO, hydration to the hemiacetal $H_2C(OH)_2$ and subsequent dehydrogenation to formic acid (HCOOH) could take place as shown in entry 3 (the overall reaction $CH_3OH + H_2O \rightarrow HCOOH + 2\ H_2$ is shown in entry 4). Formic acid is by itself an interesting hydrogen source and decomposes further to CO_2 and H_2. In summary, entry 6 shows the conversion of a 1 : 1 mixture of methanol and water which delivers inert CO_2 and three equivalents of H_2 (12 wt%) leading ideally to $\Delta E_F = -672$ $KJmol^{-1}$. Entries 7 and 8 show self-condensation reactions of methanol which also proceed under liberation of hydrogen and no formation of CO. Further interesting fuel combinations consist in mixtures of methanol and ammonia which give formamide, $HCONH_2$, and two equivalents of H_2 (8.1 wt%). The reaction shown in entry 10 is a side reaction to be expected and of lower interest because only 4.1 w% of H_2 are liberated and the resulting imine $H_2C{=}NH$ would oligomerize.

Ethanol is easily generated from biomass feedstock. This process requires the conversion of starch into maltose, followed by metabolisms into ethanol and CO_2. The emerging technology based on the direct fermentation of cellulose has the potential to produce ethanol from biological waste at competitive prices with gasoline. If this new feedstock materializes, ethanol may serve as thermal or photosynthetic precursor to H_2. Although its hydrogen content (13 wt%) is slightly higher than the one of methanol (12.5 wt%), its complete conversion to a carbon oxide (CO or CO_2) and H_2 requires breaking of the C-C bond which is more difficult than the cleavage of C-H bonds. This adds a further challenge to an already challenging problem. In entries 11 – 16 we list reactions comparable to the ones discussed for methanol. Because of the lower gravimetric H_2 content, these reactions give a lower energy gain per mass unit. Note however that ethanol is likely a more convenient substrate for homogeneously catalyzed processes as poisonous CO formation may be easier to suppress compared to reactions with methanol. It is also a substrate which can be easily purified from other catalyst poisons like sulphur.[6]

Hydrogen production from biomass carbohydrates like sugars and polyols would achieve very low carbon emissions throughout a life cycle. Currently, the latest advance in hydrogen production from sugars involves bio-catalysis (photo-fermentation, anaerobic fermentation, electrohydrogenesis), chemical catalysis (gasification, pyrolysis, gasification in critical water and aqueous phase reforming) and combinations of these procedures. All of them give relatively low yields of hydrogen. The drastic conditions required for the chemical aqueous phase reforming (temperature > 400 K and pressure > 70 bar) have been considerably reduced by the use of metal containing heterogeneous catalysts.[7] Very few investigations focussed on the development of single site molecular catalysts to achieve this transformation with high efficiency.

Table 1. Themochemical data for hydrogen formation by dehydrogenation or dehydrogenative coupling of alcohols.

Entry	**Reaction**	**ΔH_r (kJ mol^{-1})[a]**	**H_2 wt%**	**ΔE_F (kJ mol^{-1})[a]**
1	$CH_3OH \longrightarrow H_2CO + H_2$	89.1	6.2	−152.9
2	$H_2CO \longrightarrow CO + H_2$	5.4	6.6	−236.6
3	$H_2CO + H_2O \longrightarrow HCO_2H + H_2$	-20.9	4.2	−262.9
4	$CH_3OH + H_2O \longrightarrow HCO_2H + 2\,H_2$	68.2	8.0	−415.8
5	$HCO_2H \longrightarrow CO_2 + H_2$	-14.9	4.3	−256.9
6	$CH_3OH + H_2O \longrightarrow CO_2 + 3\,H_2$	53.3	12.0	−672.7
7	$2\,CH_3OH \longrightarrow HCO_2CH_3 + 2\,H_2$	54.5	6.2	−429.5
8	$3\ CH_3OH \longrightarrow CH_3OCH_2OCH_3 + H_2 + H_2O$	26	2.1	−216
9	$CH_3OH + NH_3 \longrightarrow HCONH_2 + 2\,H_2$	64.9	8.1	−419.1
10	$CH_3OH + NH_3 \longrightarrow CH_2{=}NH + H_2 + H_2O$	120	4.1	−122
11	$CH_3CH_2OH \longrightarrow CH_3CHCO + H_2$	63.3	4.3	−178.7
12	$CH_3CHO + H_2O \longrightarrow CH_3CO_2H + H_2$	−20.5	3.2	−262.5
13	$CH_3CH_2OH + H_2O \longrightarrow CH_3CO_2H + 2\,H_2$	42.8	6.2	−441.2
14	$2\,CH_3CH_2OH \longrightarrow CH_3CO_2CH_2CH_3 + 2\,H_2$	22.6	4.3	−461.4
15	$CH_3CH_2OH + NH_3 \longrightarrow CH_3CONH_2 + 2\,H_2$	41.6	6.3	−442.4
16	$CH_3CH_2OH + 3\,H_2O \longrightarrow 2\,CO_2 + 6\,H_2$	172.4	12	-1280
17	$(CH_3)_2CHOH \longrightarrow (CH_3)_2C{=}O + H_2$	37.5	3.3	−204.5

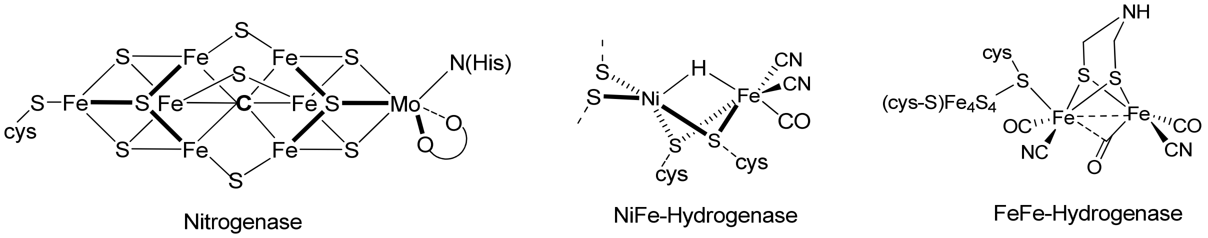
[a] *NIST values: http://webbook.nist.gov/chemistry/*

2. *Hydrogen production from alcohols in biological systems*

In photosynthesis, carbohydrates are produced by reduction of carbon dioxide, while O_2 is released by the oxidation of water. The (solar) energy stored in carbohydrates (or their metabolic products) can be released in fermentation processes which produce H_2 under anaerobic conditions. In such fermentation processes, the carbohydrates are converted to oxygenated products (aldehydes, carboxylates, CO_2) under the formal production of protons as oxidation equivalents. The biological hydrogen production is fundamentally dependent upon nitrogenase and FeFe- or NiFe-hydrogenase enzymes that catalyse the reduction of these protons (Eq. 18).

$$\text{Eq. 18} \quad 2\,H^+ + 2\,e^- \rightleftharpoons H_2$$

Only key-features of enzymatic catalytic systems will be mentioned in this article. All known enzymes which are able to catalyse hydrogen evolution contain metallo clusters as active sites. Nitrogenase is a two component system that uses a Mg(ATP) complexed Fe-protein associated with a MoFe-protein which contains the Fe_7MoS_9C co-factor (FeMoco) as active site (Scheme 1)[8] and low potential electrons from reduced ferredoxin or flavodoxin to reduce protons to hydrogen.[9] The NiFe-hydrogenases are heterodimeric proteins containing a small unit consisting of two [4Fe–4S], one [3Fe–4S] cluster, a large subunit containing a dinuclear thiolate and a hydride bridged nickel iron unit. The iron centre is further coordinated to two terminal CN and one CO ligand.[10] The FeFe-hydrogenase (or Fe-only hydrogenase) contains a completely different protein structure where the active site is a Fe_2S_2 butterfly-shape core bridged by residual cysteines and the Fe atoms are coordinated to CN and CO ligands, configuring the H-cluster (Scheme 1). These metal complexes are concealed within the protein matrix while the redox mediators (e. g. ferredoxin) are bound to the protein surface and the [Fe-S] clusters ensuring the electron transfer from ferredoxin to the polymetallic active sites. These enzymes belong to the class of the most efficient catalysts known, e.g. FeFe-hydrogenase of *Desulfovibrio desulfuricans* produces 2×10^5 L of H_2 (mol enzyme)$^{-1}$ s^{-1}.[11] A simplified mechanistic proposal for proton reduction involves the active participation of the ligands coordinated to these metal centres. For the [FeFe]-hydrogenases, the first step is proposed to be the protonation of the bridging azapropanedithiolate ligand which lowers the redox potential of the H-cluster. The reduction of the protonated species results in formation of a highly reactive terminal hydride which undergoes a fast intramolecular proton-hydride interaction forming molecular hydrogen. As for the [NiFe]-hydrogenases, protonation is proposed to occur at the sulphur of a terminal or bridging cysteine ligand, and the redox active centre has been assigned to Ni rather than to the Fe centre.[12] In Nitrogenases the mechanism at the FeMoco is not well understood. The reported data disfavours any model that involves protonation of sulphur sites and suggests that the intermediate instead contains two chemically equivalently bound hydrides; it appears unlikely that these are terminal monohydrides.[13]



Scheme 1. Active sites of nitrogenase and hydrogenases enzymes

2.1. Photofermentation

Photoheterotrophic H_2 production or photofermentation uses metabolic products from glucose as electron donors. The mechanistic pathway of photofermentation has been studied in purple non-sulfur bacteria (PNSB). Under anaerobic conditions, electron transfer for organic substrates to oxidized ferredoxin (Fdox) occurs through a series of membrane-bound electron transport carrier molecules, promoting the reduction of molecular dinitrogen to NH_3. Nevertheless, in the absence of N_2, nitrogenase catalyses instead the reduction of protons to H_2 according to Eq. 19. The key aspects that affect the efficiency of H_2 production are currently under investigation.[14]

$$\text{Eq. 19} \quad 8\,H^+ + 8\,e^- + 16\,\text{ATP} \xrightarrow[h\nu]{\text{Nitrogenase}} 4\,H_2 + 16\,\text{ADP} + 16\,\text{Pi}$$

2.2. Dark fermentation

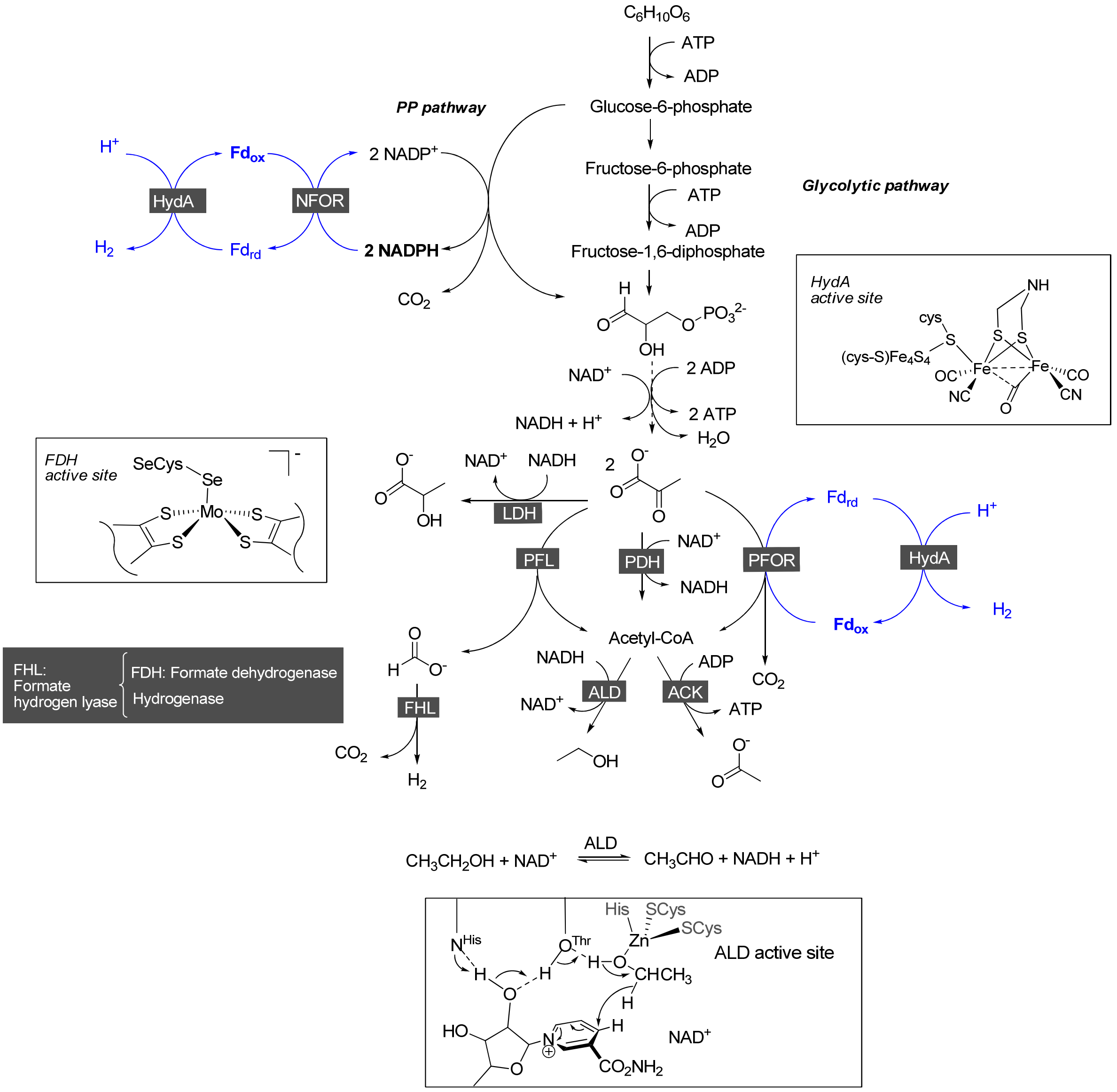
This process is mostly carried out by species of bacteria, protozoa and fungi that live in anaerobic environments without light. Carbohydrates (mainly glucose) are the preferred carbon sources for the dark fermentation process where hydrogen together with volatile fatty acids are generated.[15] Eq. 20 shows the maximal theoretical yield of 4 mol H_2/mol glucose which is produced in dark fermentation (Thauer limit).[16]

$$\text{Eq. 20} \quad C_6H_{12}O_6 + 2\,H_2O \rightleftharpoons 2\,CH_3CO_2^- + 2\,CO_2 + 4\,H_2 + 2\,H^+$$

Oh *et al.*[17] proposed three types of biochemical reactions involved in the dark fermentation process (Scheme 2). The first one employs pyruvate formate lyase (PFL) and formate hydrogen lyase (FHL). Pyruvate is formed in the Embden-Meyerhof-Parnas (EMP) pathway and is converted by PFL into acetyl-CoA and formate under anaerobic conditions. Formate is then converted into H_2 and CO_2 by the action of FHL, a complex consisting in two metalloenzymes: formate dehydrogenase and hydrogenase. The formate dehydrogenase (FDH) contains an active centre with a Mo atom coordinated to two ene-dithiolate ligands. The second type of H_2-producing reaction involves pyruvate ferredoxin oxidoreductase (PFOR) and ferroxin-dependent hydrogenase (HydA). PFOR catalyses the oxidative decarboxylation of pyruvate to form acetyl-CoA and CO_2 under anaerobic conditions. The electrons are first transferred to Fd_{ox}, and from the reduced form are then transferred to protons to form H_2. The third type of reaction utilizes NAD(P)H to evolve H_2 and is catalyzed by two major enzymes, NAD(P)H: ferredoxin oxidoreductase (NFOR) and HydA. In this reaction, Fd_{ox} is reduced by NAD(P)H, which is formed during the carbon metabolism.

Alcohol Dehydrogenase (ALD) with coenzyme nicotinamide adenine dinucleotide (NAD), catalyzes the reversible oxidation of ethanol to acetaldehyde. A close-up of the active site of ALD is shown in Scheme 2 where a Zn centre is coordinated to two cysteine and a histidine residues. ADH utilizes a Zn^{2+} ion to coordinate the alcohol oxygen and increase the acidity of the hydroxy group. During activation, a sequential proton transfer from a threonine to a histidine residue through NAD^+ takes place. The resulting anionic Thr accepts then a proton from the alcohol substrate while the NAD^+ receives a hydride forming NADH and a molecule of aldehyde. This represents an archetypical example where the metal and a ligand cooperate and their interplay facilitates a transfer hydrogenation process. This principle has direct implications in the development of enzymatic fuel cells and *direct alcohol organometallic fuel cells* using biomimetic models (see section 3.2.1).

Dark fermentative H_2 production reminds of the fermentative methane (CH_4) production. This simplest hydrocarbon (with a gravimetric hydrogen content of 25%) is produced in the anaerobic digestion of organic wastes and biological production processes have been well established commercially. H_2 is more valuable as an energy source but the development of a similar biofermentation process still needs to be improved with respect to the yield of H_2 which is currently too low. To increase productivity and efficiency, detailed studies of the H_2 metabolism are essential which will eventually allow engineering microorganisms at the cellular level to optimize the H_2 yield. First encouraging results reveal an enormous potential for improving the H_2 yield in the transformation of organic substrates (alcohols, sugars, acids).[18]



Scheme 2. Metabolic pathway for H_2 production during glucose fermentation in *E. coli* and Enterobacteriaceae. Additional pathways to improve H_2 yield were introduced by Veit *el al.*[19] and Jones *el al (in blue)*.[20] Active sites of ferredoxine-dependent hydrogenase, formate dehydrogenase and alcohol dehydrogenase are indicated. ACK: acetate kinase; ALD: alcohol dehydrogenase; Fd_{ox}: oxidized ferredoxin; Fd_{rd}: reduced ferredoxin; FHL: formate hydrogen lyase; HydA: ferredoxin-dependent hydrogenase; LDH: lactate dehydrogenase; PP pathway: pentose phosphate pathway; NFOR, NAD(P)H: ferredoxin oxidoreductase; PDH: pyruvate dehydrogenase; PF:, pyruvate formate lyase; PFOR: pyruvate:ferredoxin oxidoreductase. (Adapted from Ref 17)

Structural and electronic features of these biocatalytic systems inspired the search for artificial molecular catalysts during the past decade. These models frequently use established reaction steps from organometallic chemistry like oxidative insertion or nucleophilic substitution, β-hydrogen elimination, and reductive elimination to explain and plan a reaction mechanism for hydrogen production from sugars. More recent studies have also taken the coordination of functional ligands into account that cooperate with the metal to facilitate the reactions that lead to H_2 production.[21]

3. Hydrogen production from alcohols in artificial systems

The focus of this review is on homogenous catalytic systems and we only very briefly mention progress made with heterogeneous catalysts and refer to the recent literature for detailed reviews.[22]

3.1 Heterogeneous catalysis for dehydrogenation of alcohols

3.1.1 Electro-oxidation of alcohols

Although proton exchange membrane fuel cells (PEMFC) due to their low operating temperature can be used as suitable power sources for automotive applications,[23] storage of hydrogen as fuel in liquid form or as gas under high pressure in a vehicle is considered to be potentially dangerous. Here we mention only very briefly some concepts used in heterogeneous electro-oxidation of methanol and refer to the articles dedicated to this particular topic.[24]

Alcohols which are liquid under ambient conditions can be used as instant fuel in the so called "Direct Alcohol Fuel Cell (DAFC)".

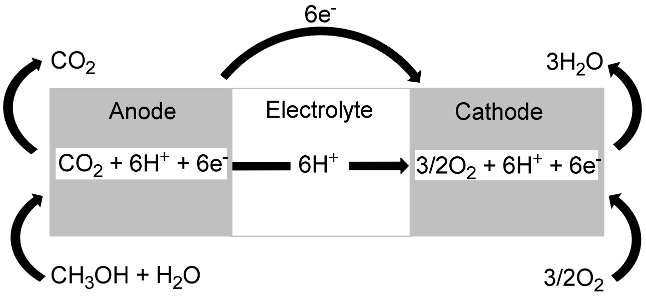


Figure 2. Simplified graphic presentation of a DMFC

Amongst different alcohols such as ethanol, 2-propanol and ethylene glycol, the direct methanol fuel cell (DMFC) (Figure 2) is the most developed system. In a DMFC, methanol is electro-oxidized to carbon dioxide at the anode, which is most commonly made from Pt. The anode reactions which are proposed to occur on a Pt electrode are represented in Scheme 3.[23a]

$$\begin{aligned}
CH_3OH + 3\ Pt(s) &\longrightarrow Pt_3\text{-}COH + 3\ H^+ + 3\ e^- \\
Pt_3\text{-}COH &\longrightarrow Pt\text{-}CO + 2\ Pt(s) + H^+ + e^- \\
Pt(s) + H_2O &\longrightarrow Pt\text{-}OH + H^+ + e^- \\
Pt\text{-}CO + H_2O &\longrightarrow Pt\text{-}COOH + H^+ + e^- \\
Pt\text{-}COOH &\longrightarrow Pt(s) + CO_2H^+ + e^-
\end{aligned}$$

Scheme 3. Proposed reaction steps for methanol oxidation on a Pt anode

Besides many advantages of a DMFC, the major drawbacks that this system still has to overcome are the slow anode kinetics, lack of selectivity, and long-term stability. Although oxidation of methanol is fast on a clean Pt anode, adsorption of carbon monoxide which is generated as an intermediate in this reaction poisons the catalyst making the overall methanol oxidation sluggish. To overcome this challenge considerable efforts have been devoted in the development of suitable anode materials to achieve high reactivity, stability and durability. Furthermore, attempts are made to reduce the costs by decreasing the amount of expensive Pt-based noble metal catalysts. Amongst different Pt-alloys with more oxophilic metals such as Pt-Sn, Pt-Ni, Pt-Cu, Pt-Mo, Pt-Au, especially Pt-Ru based catalysts have been thoroughly investigated.[25] Extensive amount of research has been dedicated for the development of DMFCs as portable low power devices and remarkable results were achieved using Pt-Ru based catalytic systems which give power densities ranging from 45 – 207 mW cm^{-2} at temperatures ranging from 25 – 70 °C.[26] The most performant DMFC for application in transportation was developed by Siemens AG (Germany) which reaches a maximum power density of 250 mW/cm^2 at 110 °C. Also ethanol has been widely explored as fuel for DAFCs.[25] The best catalysts so far are based on Pd metal. A Pd(Ni-Zn) catalyst offers power densities of 58 mW cm^{-2} at ambient temperature and 160 mW cm^{-2} at 80 °C,[27] whereas a Pd(CeO_2)/C catalyst delivers power densities of 66 mW cm^{-2} at room temperature and 160 mW cm^{-2} at 80 °C,[28] both in alkaline media.

3.1.2 Thermal dehydrogenation of alcohols

As stated above, methanol is an especially promising hydrogen source because it can be produced from renewable or fossil stocks with solar or wind based energy supply and has high H : C ratio. An established valuable method of hydrogen production consists in the steam reforming of methanol (SRM) using heterogeneous catalysts.[29] However, SRM is an endothermic process (ΔH_r = 53.3 kJ/mol; Table 1, entry 6) and hence finding reaction conditions for efficient large-scale operation might be difficult. Partial oxidation of methanol (POM; Eq. 21) is a fast reaction but shows low selectivity and it is highly exothermic (ΔH_r = -188.5 KJ/mol) which makes the control of the reaction parameters problematic. Oxidative steam reforming which is a combination of SRM and POM gives a higher hydrogen concentration in the product (Eq. 22). All methanol steam reforming processes involve first decomposition of methanol into hydrogen and carbon monoxide (Eq. 23) which is followed by a water gas shift reaction (Eq. 24) which reduces the carbon monoxide content.

Eq. 21 $CH_3OH + 1/2\ O_2 \rightleftharpoons 2\ H_2 + CO_2$ $\Delta H_r = -188.5$ kJ/mol

Eq. 22 $2\ CH_3OH + H_2O + 1/2\ O_2 \rightleftharpoons 5\ H_2 + 2\ CO_2$ $\Delta H_r = -135.2$ kJ/mol

Eq. 23 $CH_3OH \rightleftharpoons 2\ H_2 + CO$ $\Delta H_r = 94.5$ kJ/mol

Eq. 24 $CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H_r = -41.2$ kJ/mol

The most difficult task in heterogeneous steam reforming remains the reduction of the amount of CO that is produced to avoid hydrogen fuel cell poisoning. Copper based catalysts have shown good performance in SRM as well as in water gas shift reaction and have been extensively studied. The catalytic activity and stability of the catalyst are largely dependent on the homogeneity of the copper nano-particles on the surface and the surface area of the support material. To ensure the homogeneous dispersion of copper particles and enhance the stability, metal oxides are used as support materials. Besides ZnO[29] that is most commonly used, CeO[29a,30], SnO_2[31], ZrO_2[32], Cr_2O_3[33], or combinations of oxides as ZnO/ZrO_2[34], CeO_2/ZrO_2[29j, 35], Fe_2O_3[36], CoO[37], MnO[38], ZnO/NiO[39] have shown promising activity in the SRM reaction. In late 2012, a direct route for SRM was investigated avoiding formation of any syngas (CO/H_2).[40] In a single step reaction, over a $CuZnGaO_x$ catalyst, methanol was directly converted to CO_2 and H_2 without any detectable CO formation (below 1 ppm). The high selectivity of the catalytic system implies that neither decomposition of methanol to H_2 and CO (syngas formation, Eq. 23) nor a subsequent water gas shift reaction (Eq. 24) is involved in the catalytic process. A clean production of hydrogen with 393.6 ml (g catalyst)$^{-1}$ h^{-1} was reached at 150 °C.

Copper based catalysts are currently applied in industrial SRM processes although they still suffer from limitations like low thermal stability, tendency of sintering at temperatures above 270 °C, and the pyrophoric nature of copper nanoparticles.[41] Alternatively, palladium nanoparticles can be used which likewise promote the methanol decomposition to hydrogen and carbon monoxide (Eq. 23),[42] and allow the partial oxidation of methanol (Eq. 21).[43] Pd supported on ZnO shows excellent selectivity in the SRM process liberating hydrogen and carbon dioxide with very low carbon monoxide contamination. A detailed study by Iwasa *et al.* demonstrated that Pd/ZnO and copper based catalysts show very comparable activities but the Pd containing catalyst is superior in terms of long-term stability.[44] The formation of a robust Pd/Zn bimetallic alloy is made responsible for the high reactivity and stability of the Pd/ZnO catalyst and consequently this Pd/ZnO catalytic system is considered as a suitable alternative for the presently established SRM catalysts.[45] Further palladium based catalytic systems with Ga_2O_3[46] and In_2O_3[47] as support materials were studied by Penner *et al.* Also other metals than Cu and Pd were investigated and Pt-alloys[48] as well as Ni[49], Mo[50] based catalysts have been utilized for the hydrogen production from methanol. Recently, Shimizu *et al.* explored the heterogeneous dehydrogenation of cyclic secondary alcohols using Co/TiO_2 and Ni/Al_2O_3 catalyst which led to promising results.[51]

Likewise, ethanol steam reforming is of great interest because ethanol is non-toxic, liquid, an easy-to-handle fuel and may become available on large scale from plant waste. Ideally, the steam reforming of ethanol produces six molecules of hydrogen gas and two equivalents of CO_2 per molecule of ethanol (entry 16 in Table 1). Indeed, hydrogen production from ethanol has been extensively investigated during the last couple of years and interested readers are referred to the reviews by Fernando[52] Fierro[29p] Homs[53] Weckhuysen and Bruijnincx[54] as well as to a recent report by Schmidt *et al*.[55]

Furthermore, a report from Cuenya *et al* gives an excellent account concerning the decomposition of ethanol and higher order alcohols such as 2-propanol and 2-butanol over platinum nanoparticles supported on ZrO_2 which leads to the production of hydrogen gas.[56]

3.1.3 Photocatalytic decomposition of alcohols

The energy needed to promote the endothermic dehydrogenation of alcohols to form hydrogen alongside aldehydes, ketones and carboxylic derivatives as dehydrogenated (oxidized) organic molecules can be provided by light (photons). In these processes semiconductors can be used as catalysts in order to lower the activation barriers of the photolytic reactions steps. Since the first experiments reported by Fujisima and Honda, the photocatalytic hydrogen production from water is one of the most promising approaches.[57] After the first reports which described the use of TiO_2 as photocatalyst, a large number of other semiconducting metal oxides and sulfides (CdS, ZnO, ZrO_2, titanates, niobates, and tantalates) have been identified to have suitable properties (band gaps of ca. 3 eV and conduction bands in the range of −2 to −1 V for proton reduction in aqueous media) for the photocatalytic splitting of water using UV light. Visible-light-responsive photocatalysts are accessible by coupling a wide band gap semiconductor (e.g TiO_2 3.2 eV) with a narrow one (CdS 2.44 eV, In_2S_3 2.1 eV) as a sensitizer.[58] It has been demonstrated that the rate of hydrogen production from alcohol/water mixtures is much higher compared to that from pure water. Under irradiation, the TiO_2-promoted photocatalytic reaction is initiated by charge-separation into electrons (e) and holes (h^+) with photons of energy equal or higher than the band gap. The electrons injected into the conduction band reduces water to generate H_2 while the remaining h^+ in the valence band oxidizes the hydroxide ions (HO^-), to give a highly reactive $HO^\bullet$ radical.[59] With alcohols as sacrificial electron donors, the reaction is accelerated since they are not only consumed by the photogenerated holes but they react also rapidly with the photogenerated $HO^\bullet$ radicals thereby decreasing the rate of electron-hole recombination and suppressing the "Knallgas" reaction between photogenerated H_2 and O_2 which both lower the quantum yield of the H_2 production.[60] Methanol plays a crucial role as sacrificial donor for the hydrogen production from water and its photochemistry has been extensively investigated on single-crystalline TiO_2 surfaces[61] and on TiO_2 powders.[62] Although little is known about the mechanistic details, these studies show that beside hydrogen, formaldehyde, formic acid and carbon dioxide are the further oxidation products generated from methanol.[63] Noble metal deposits including Pt, Au, Pd, Rh, Ni, Cu and Ag have been reported to enhance significantly the efficiency of TiO_2 mediated photocatalysis. The Fermi levels of these noble metals lie below that of TiO_2 and photo-excited electrons are efficiently injected from the TiO_2 conduction band to the metal particles deposited on the surface of TiO_2. The photo-generated holes remain in the valence band of the TiO_2. This modification reduces significantly electron-hole recombination, enhances the life time of the charge separated state of the photocacalyts, and thereby raises the photocatalytic yield in the reduction of protons to H_2.[64]

To date there are only few reports on the photocatalytic reforming of biomass to hydrogen. The first attempt of a photocatalytic conversion of saccharides was reported by Kawai *et al*. who showed that hydrogen could be generated from starch or cellulose on a complex Pt (5% wt)/RuO_2 (10% wt) / TiO_2 photocatalyst using a 500 W Xe lamp as photon source which gave turn over numbers (TONs) of about 43 (Scheme 4).[65]

$$(CH_2O)_n \; + \; n\,H_2O \xrightarrow[h\nu]{RuO_2/TiO_2/Pt} 2n\,H_2 \; + \; n\,CO_2 \text{ (or } NaCO_3\text{)}$$

neutral or basic

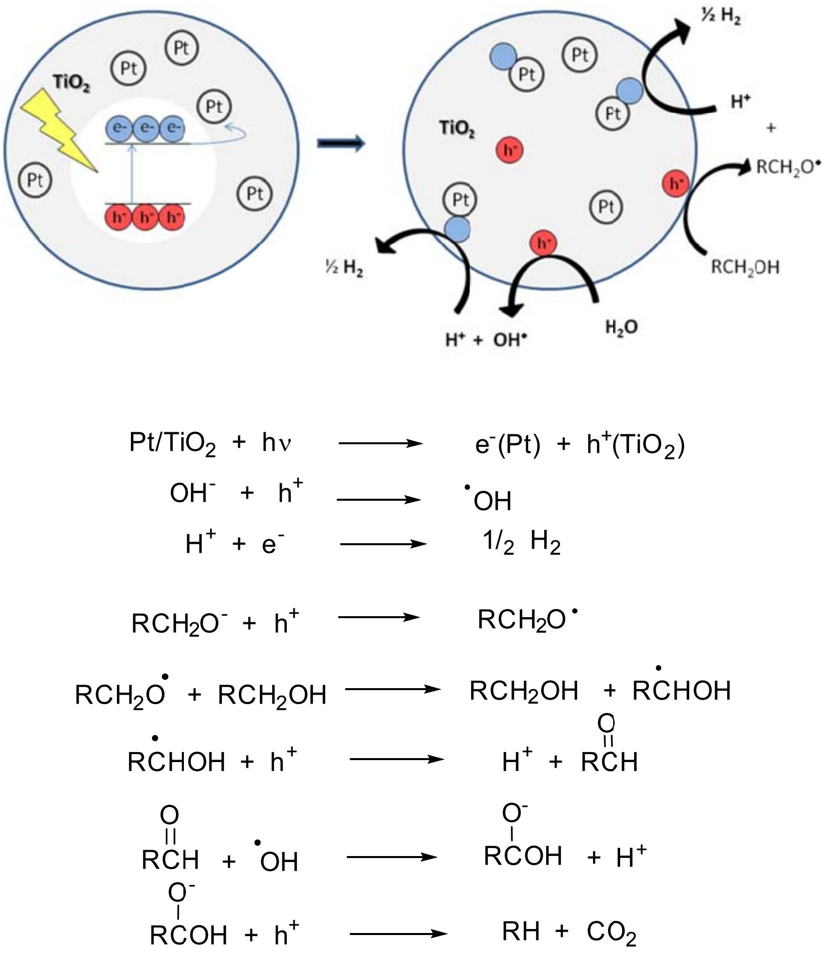
TON 43

	H_2 (μmol h^{-1})	CO_2 (μmol h^{-1})	QY at λ= 380 nm (%)
saccarose (n = 12)	14 (17)*	7	1.2 (1.5)*
starch (n = 600)	10 (16)*	5	0.8 (1.3)*
cellulose (n = 2000-10000)	3.5 (12)*	2	0.3 (1.0)*

* (NaOH 6M)

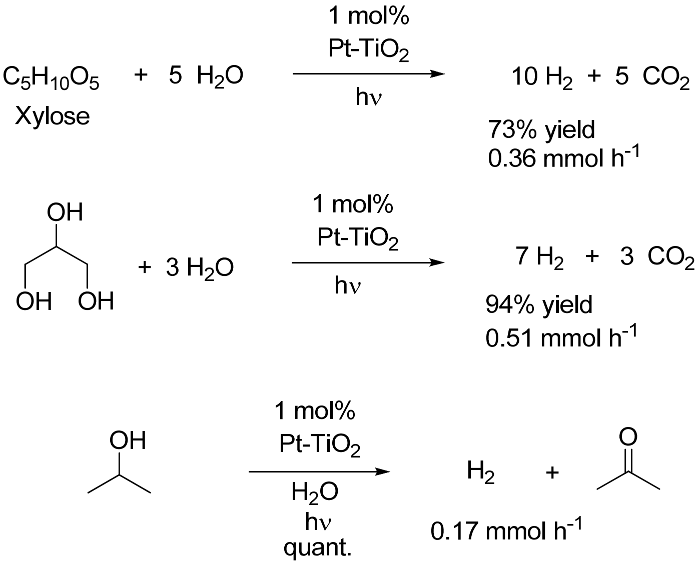
Scheme 4. H_2 and CO_2 evolution from sugar mixtures with the photocatalyst Pt/RuO_2/TiO_2 suspended in neutral water or 6 M NaOH solution.

Fu *et al*. reported that Pt-doped TiO_2 (Pt 1 %wt/TiO_2) catalyses the photochemical H_2 evolution using a hexose as a sacrificial reagent with a maximum rate of hydrogen evolution of 0.28 mmol h^{-1}. The performance of the catalytic system is highly dependent on the pH of the solution and under the strictly anaerobic conditions a TON = 108 is achieved.[66] A highly speculative reaction mechanism proposed by the authors is represented in Scheme 5. It is assumed that photo-reduced Pt nanoparticles react with solvated protons to give H_2 while hydroxide and alkoxide anions are oxidized to highly reactive oxy radicals from whom carbonyl compounds (aldehydes, ketones, carboxylic acids) and hydrocarbons are produced. Yasuda *el al.* implemented this process for the photo-degradation of pentoses in order to develop an efficient method to produce H_2 from cellulosic materials.[67] The same authors reported recently that also other polyols (eritryol or glycerol) serve as sacrificial multi-electron donors and allow the quantitative decomposition into CO_2 and H_2O using a similar photocatalytic system (Scheme 6).[68]



$$Pt/TiO_2 + h\nu \longrightarrow e^-(Pt) + h^+(TiO_2)$$
$$OH^- + h^+ \longrightarrow {}^{\bullet}OH$$
$$H^+ + e^- \longrightarrow 1/_2\ H_2$$
$$RCH_2O^- + h^+ \longrightarrow RCH_2O^{\bullet}$$
$$RCH_2\dot{O} + RCH_2OH \longrightarrow RCH_2OH + R\dot{C}HOH$$
$$R\dot{C}HOH + h^+ \longrightarrow H^+ + R\overset{\overset{O}{\|}}{C}H$$
$$R\overset{\overset{O}{\|}}{C}H + {}^{\bullet}OH \longrightarrow R\overset{\overset{O^-}{|}}{C}OH + H^+$$
$$R\overset{\overset{O^-}{|}}{C}OH + h^+ \longrightarrow RH + CO_2$$

Scheme 5. Proposed mechanism for the photocatalytic reforming of glucose on Pt/TiO_2 by Fu *et al.* (Adapted from reference 66)



Scheme 6. Photocatalytic H_2 evolution from pentose, glycerol or 2-propanol using Pt-TiO_2 under neutral conditions.

In their pioneering experiments, Grätzel *et al.* described a hybrid system composed from hydrogenase enzymes and an inorganic light-harvesting support. Three different redox enzymes fixed to TiO_2 as semiconducting support were able to catalyse the H_2 production under excitation of the band gap in the presence of MeOH as electron donor. The H_2 formation was obtained by direct electron transfer from the conduction band of the TiO_2 particles to the active site of the enzyme at pH > 7. In addition, rhodium polypyridyl complexes were used to enhance the efficiency of the electron transfer from the TiO_2 particles to the adsorbed enzyme. The maximum rate of hydrogen evolution was 1.42 mmol (g^{-1} TiO_2) h^{-1} in the presence of $[Rh(bpy)_3]^+$.[69]

3.2 Dehydrogenation of alcohols under acceptorless conditions using molecular catalysts

3.2.1 Electrocatalytic oxidation of alcohols

The production of hydrogen from alcohols is intimately connected with the reversible generation of electric current and protons via the equation $H_2 \leftrightarrows 2\ H^+ + 2\ e^-$ and for that reason we list here selected examples where alcohols were electrocatalytically dehydrogenated (oxidized) with molecular catalysts although these reaction do not produce hydrogen directly (see also the short discussion in section 2 on hydrogenases).[70] Besides the heterogeneous catalysts used for direct alcohol fuel cells as discussed in Sec. 3.1.1, fuel cell design has embarked into a new direction with the development of molecular catalysts for electro-oxidation. The molecular catalyst can be used in two different ways: Either it is dissolved in the electrolyte and catalyses a reaction in homogeneous solution (Figure 3A) or is heterogenized by embodiment into the electrode surface (Figure 3B).[71]

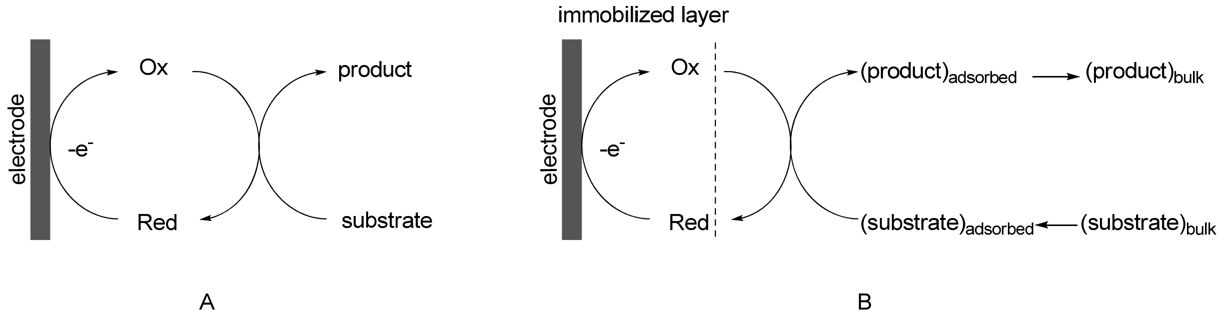
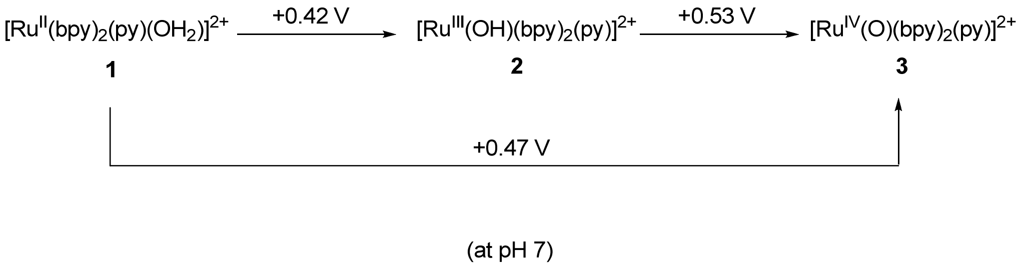


Figure 3. Electrocatalytic oxidations

An advantage of molecular catalysis is that it leaves large room for improvements through the design of the active species with the use of different metals and ligands. Moreover, a defined catalytic system offers the opportunity of developing an understanding of the mechanistic details. Savéant *et al.* has classified homogeneous electrocatalysis into two categories: a) redox catalysis where the catalyst couple plays only the role of an electron carrier, and b) chemical catalysis where temporary catalyst-substrate adduct formation takes place.[72] Ruthenium and nickel based electrocatalysts were extensively reviewed by Wong *et al.* in 2007[71] and hence, we will detail here only the molecular electrocatalysts that were developed afterwards. The most commonly used molecular catalysts are based on ruthenium and more specifically, ruthenium-oxo complexes are most frequently used. In the eighties of the last century, Meyer *et al.* developed versatile synthetic routes for high-valent ruthenium(IV)-oxo complexes and applied them in the catalytic electro-oxidation of alcohols.[73] In aqueous solution, $[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ (**1**) can be reversibly converted to the high valent $[Ru^{IV}(O)(bpy)_2(py)]^{2+}$ oxo complex (**3**) by 2e⁻ oxidation (Scheme 7) which then oxidizes alcohols electrocatalytically.



Scheme 7. Redox reaction of the Ru-polypyridyl complex

Over the last decades, different research groups focused on the modification of the ligand structure and specifically investigated various polypyridyl ligands (**L1**-**L7**, **L9** and **L11**). Other ligand types like [9]aneS3 (**L8**) were less intensely studied (see Figure 4).[74] Many of these complexes with the polyaromatic ligand AC (**L10**) or the polypyridyl ligand bpy* (**L11**), etc. (Figure 4) are adsorbed on the electrode surface and act as heterogenized catalysts according to a system of type 3B in Figure 3.

Generally, these Ru(IV)-oxo complexes suffer from low stability, low product selectivity and gave rather low rates of conversion.[71]

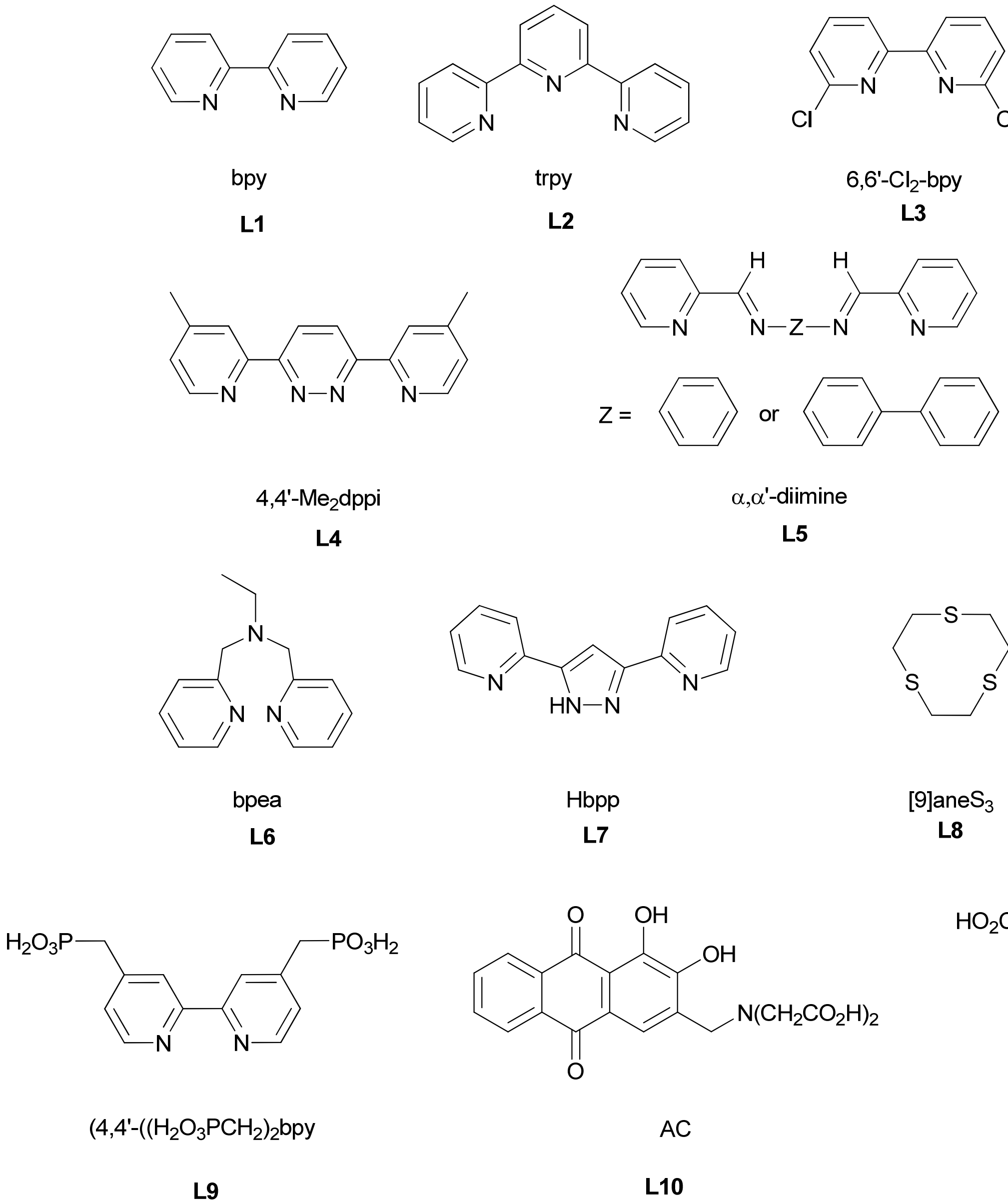
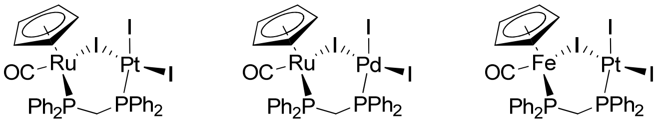


Figure 4. Ligands used in Ru catalyzed electro-oxidation

Ruthenium-dioxolene-amine complexes were studied by Tanaka *et al.* and these were able to oxidize alcohols under electrocatalytic conditions, although they fell short in product selectivity and did not generate high current densities.[75] Heterobimetallic Ru/Pt (**4**), Ru/Pd (**5**), and Fe/Pt (**6**) cyclopentadienyl carbonyl complexes (Figure 5) have been utilized as soluble electrocatalysts in the oxidation of alcohols by McElwee-White *et al.*[76] However, in the electrocatalytic dehydrogenation of methanol and ethanol, these complexes showed poor product selectivity and gave a mixture of products including aldehyde, acid and ester.



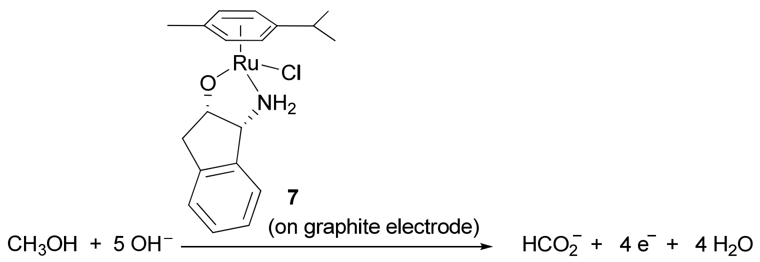
4 5 6

Figure 5. Heterobimetallic complexes used in the electro-oxidation of alcohols

In this context, it is worth mentioning that in a conceptually related approach bimetallic homogeneous Ru/Ni complexes have been successfully utilized in hydrogen fuel cells by Ogo *et al.* although again with low current densities.[77]

Meyer *et al.* have reported the electrocatalytic oxidation of benzyl alcohol promoted by a polypyridyl ruthenium(V)-oxo complex and they were able to identify a number of intermediates.[78] This particular complex $[Ru(Mebimpy)(4,4\text{-}\{(H_2O_3PCH_2)_2bpy\}(OH_2)]^{2+}$ [Mebimpy = 2,6-bis(1-methylbenzimidazol-2yl)] is equipped with a phosphonate-modified bipy ligand $[4,4\text{-}(H_2O_3PCH_2)_2bpy]$ (**L9** in Figure 4) and is attached to a nanostructured ITO surface leading to a catalyst of type 3B in Figure 3. This device works as electrocatalyst in the water oxidation reaction. Four distinct intermediates were observed during water oxidation, namely $Ru^{IV}{=}O^{2+}$, $Ru^{IV}(OH)^{3+}$, $Ru^{V}{=}O^{3+}$ and $Ru^{V}(OO)^{3+}$ species, each of them were found to be active in the electro-oxidation of benzyl alcohol to form benzaldehyde as the major product (up to 66% Faradaic efficiency). In case of the nanoITO/$Ru^{V}(OO)^{3+}$ catalytic system, a TON of 2440 was obtained and the catalytic activity improved by a factor of 3000 as compared to the $Ru^{IV}{=}O^{2+}$ species.

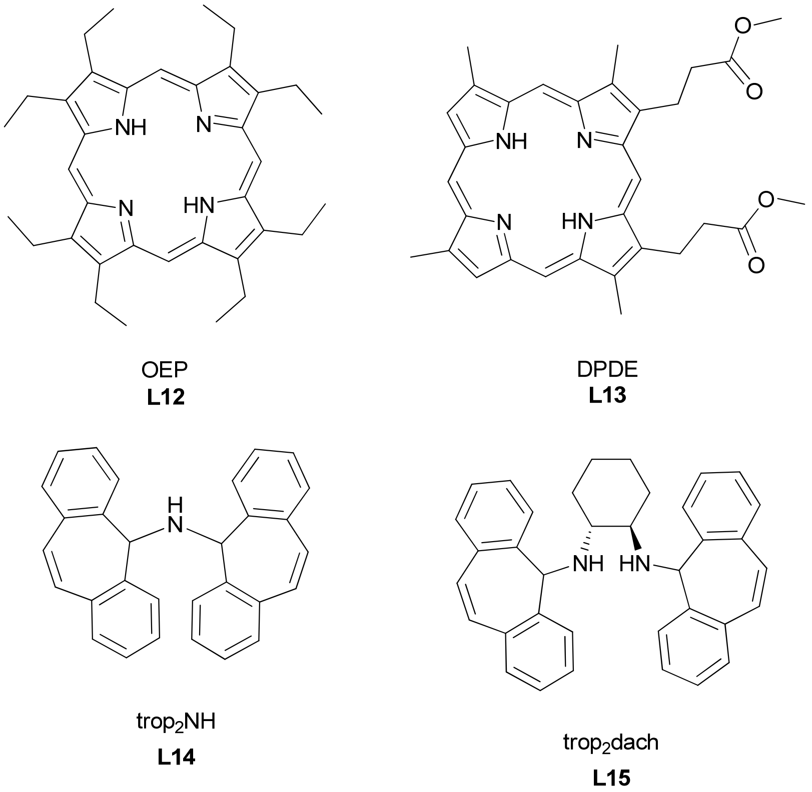
Waymouth *et al.* could successfully apply the cymene ruthenium complex **7** in the electrocatalytic oxidation of methanol.[79] Complex **7** was supported on edge-plane graphite (EPG) electrode and showed activity in the alcohol oxidation in alkaline aqueous solution (Scheme 8).



Scheme 8. Ru-catalyzed electro-oxidation of methanol

The amido alcohol complex **7** oxidizes methanol by four electrons to formate at a rate of 1.35 $M^{-1}\,s^{-1}$ (1 turnover s^{-1}). Mechanistic studies reveal that the reaction is promoted by a graphite supported Ru(IV)-oxo complex.

Seok *et al.* studied the electrochemical properties of rhodium polypyridyl oxo complexes.[80] The oxidation of the structurally elucidated complexes $[Rh^{III}(bpy)(trpy)(OH_2)]^{3+}$ and $[Rh^{III}(phen)(trpy)(OH_2)]^{3+}$ by Ce(IV) afforded the spectroscopically characterized oxo-complexes $[Rh^{V}(O)(bpy)(trpy)]^{3+}$ and $[Rh^{V}(O)(phen)(trpy)]^{3+}$, speculated as the first examples of Rh(V) complexes. The authors used the complex $[Rh^{III}(phen)(trpy)(OH_2)]^{3+}$ in homogeneous electro-oxidation of benzyl alcohol to benzaldehyde (TON up to 13). Significantly better results were achieved very recently with rhodium porphyrin catalysts. Yamazaki *et al.* immobilized the complex $[Rh^{III}(Cl)(OEP)]$ (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato; **L12** in Figure 6) on carbon black and applied this system as anode in the oxidation of ethanol in an alkaline medium.[81] Other alcohols such as methanol, propanol, 2-propanol, and benzyl alcohol derivatives also underwent electro-oxidation promoted by $[Rh^{III}(Cl)(OEP)]/C$ at a low-over-potential. The oxidation of benzaldehyde afforded a mixture of benzoic acid and benzyl alcohol. Current densities were relatively low and found to be significantly dependent on the nature and the concentration of the alcohol ranging from 1.2 to maximal 4.8 mW cm^{-2}.



OEP
L12

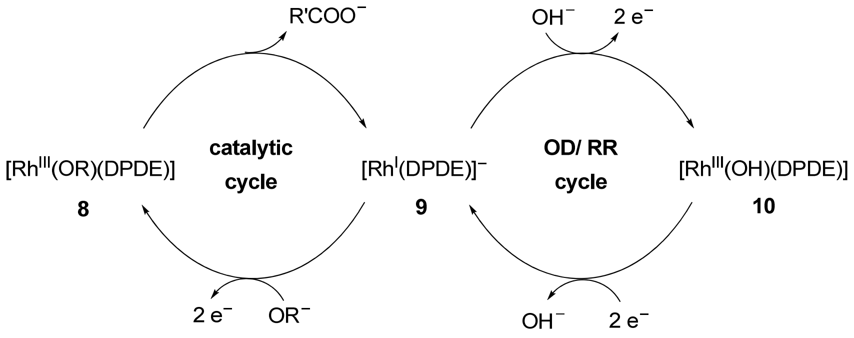
DPDE
L13

trop$_2$NH
L14

trop$_2$dach
L15

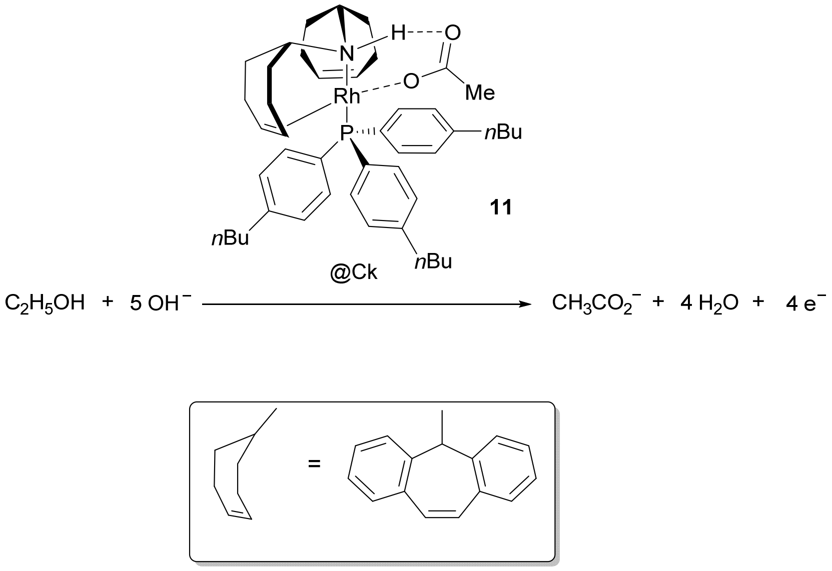
Figure 6. Ligands used in Rh and Ir catalyzed electro-oxidation

Another electrocatalytically active rhodium porphyrin complex has been recently described by Cosnier *et al.*[82] The rhodium(III) complex with the deuteroporphyrine dimethylester ligand (DPDE; **L13** in Figure 6) immobilized on a multi-walled carbon nanotube (MWCNT)/ Nafion support served as anode in a glucose fuel cell. At alkaline pH, the two electron redox-couple Rh^{I}(DPDE) / Rh^{III}(DPDE) oxidized glucose to gluconate. The experimental findings indicate an oxidative deactivation/ reductive reactivation (OD/ RR) mechanism which is likely operative in this catalytic electro-oxidation (Scheme 9). At high pH glucoxide and hydroxide ions compete in the coordination with the oxidized form of the rhodium complex and the formation of the [Rh^{III}(OH)(DPDE)] (**10**) deactivates the catalytic cycle. However, the catalyst is regenerated by the reduction of [Rh^{III}(OH)(DPDE)] (**10**) to [Rh^{I}(DPDE)]$^{-}$ (**9**). On the other hand, the glucoxide complex [Rh^{III}(OR)(DPDE)] (**8**) with OR representing deprotonated glucose oxidizes this molecule to gluconate and completes the catalytic cycle forming **9**. This molecular catalyst based glucose/O_2 fuel cell delivers a power density of 0.182 mW cm^{-2} at 0.22 V and an open circuit voltage of 0.64 V.



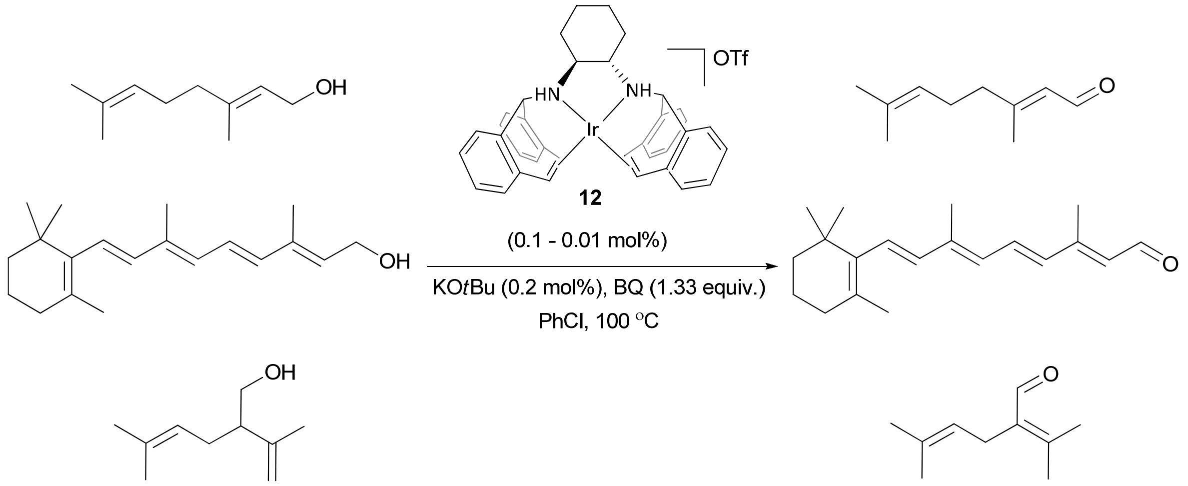
Scheme 9. Proposed mechanism for Rh-catalyzed oxidation of alcohol

Bianchini, Vizza, Grützmacher *et al.* reported a highly selective conversion of ethanol to acetate catalyzed by a rhodium(I) amido complex [Rh(trop$_2$N)(PR$_3$)] which is assessed with the diolefin amine ligand trop$_2$NH (**L14** in Figure 6).[83] Different support materials as well as rhodium(I) complexes with different combinations of phosphine ligands and counter ions were tested. Complex **11** [Rh(trop$_2$N){P(4-*n*BuPh)$_3$}][OAc] deposited on Ketjenblack EC-600JD (Ck) worked as an excellent anode catalyst in a DAFC fuel cell for the oxidation of ethanol affording up to 45% conversion and remaining active in three consecutive galvanometric cycles with catalyst loading as low as 0.1 mg cm^{-2} (Scheme 10). This example represents the highest specific activity (10000 A g_{Rh}^{-1}) achieved in a half cell for ethanol electro-oxidation up to date. The system delivers a power density of 18 mW cm^{-2} and TON = 3850 at 60 °C in an active cell which used a Fe/Co/C cathode exposed to air.



Scheme 10. Electro-oxidation of ethanol using Rh-complex **11**

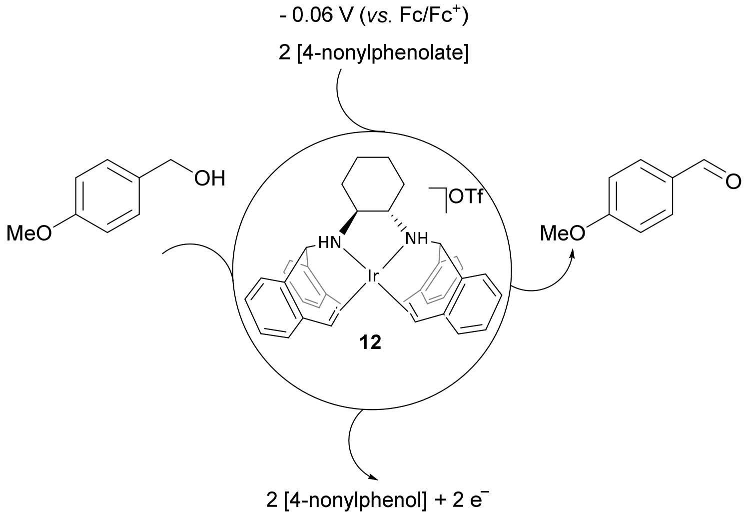
The [Ir(trop$_2$DACH)][OTf] iridium complex (**12**) with the related diamino diolefin ligand trop$_2$dach (**L15** in Figure 6) was reported to be an excellent catalyst for the highly chemoselective conversion of a broad range of primary alcohols into aldehydes.[84] Using very low catalyst loadings (0.01 mol%) in the presence of benzoquinone as hydrogen scavenger and catalytic amounts of base, the product aldehydes were obtained in good to excellent yields. This catalyst was also successfully employed for the dehydrogenative oxidation of allylic alcohols in presence of an external oxidant and catalytic amounts of base (Scheme 11).[85]



Scheme 11. Ir-catalyzed highly selective oxidation of allylic alcohols

Inspired by these results, Bonitatibus *et al.* applied **12** as a homogeneous electro-oxidation catalyst for the dehydrogenation of alcohols.[86] For example, the dehydrogenative oxidation of 4-methoxybenzyl alcohol using Grützmacher's catalyst **12** at an applied potential of –0.06 V (*vs.* Fc/Fc$^+$)

during 20 h gave 32% of *p*-anisaldehyde (Scheme 12). Running the electrolysis for 96 h led the aldehyde in 64% yield which corresponds to a Faradaic efficiency of 94%.



Scheme 12. Electro-oxidation of alcohol catalyzed by Ir-complex **12**

3.2.2 Acceptorless thermal dehydrogenation of alcohols

3.2.2.1 Transformations* catalyzed *by Ru-complexes

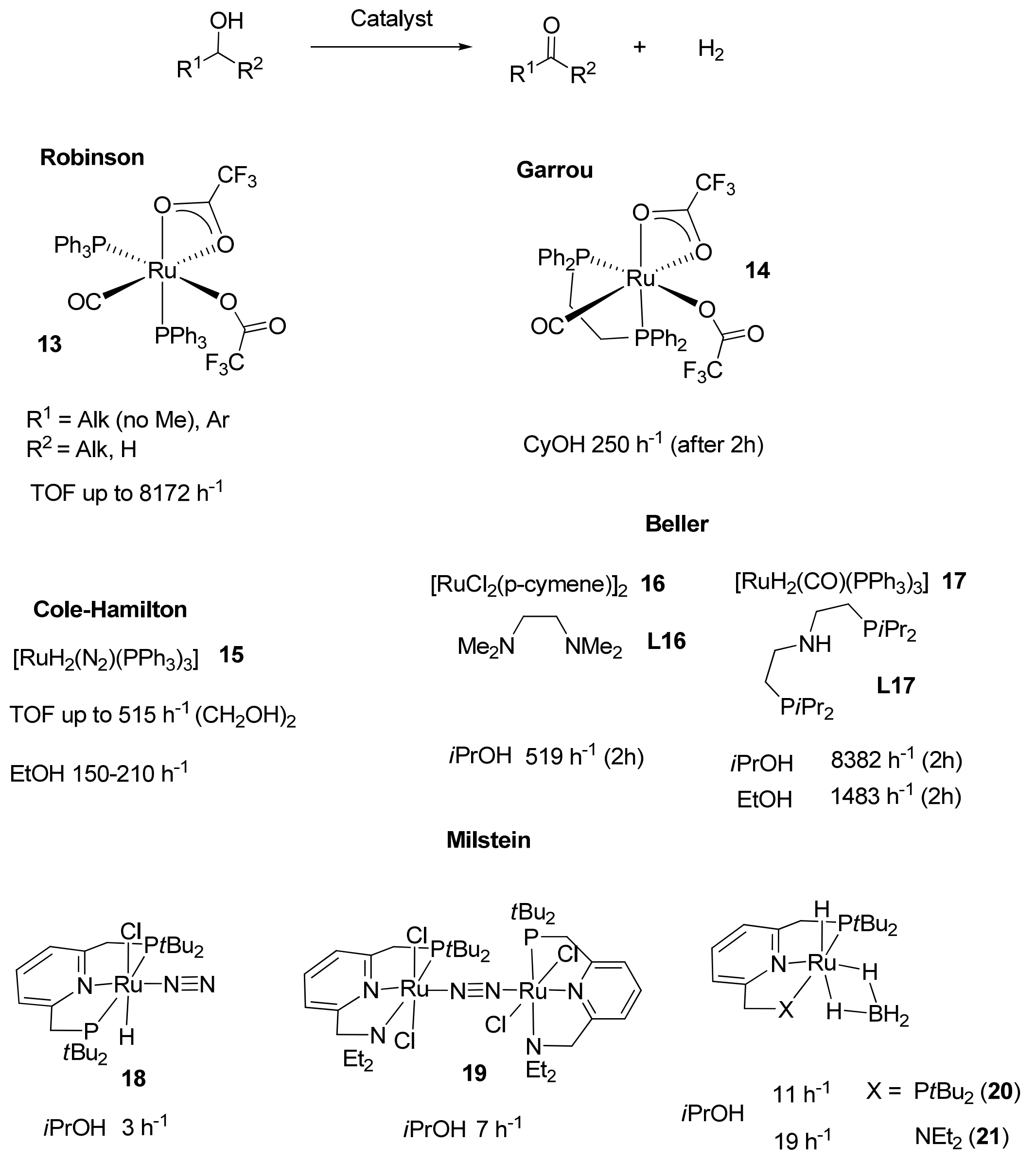
Dehydrogenation of alcohols to aldehydes and ketones

The dehydrogenation of alcohols under homogeneous conditions to provide hydrogen gas and functionalized organic molecules (aldehydes, ketones and/or carboxylic acid derivatives) has been especially successfully achieved with Ru complexes. An early example of an acceptorless dehydrogenation - that means hydrogen is directly liberated and not transferred to an acceptor molecule - of alcohols was reported by Robinson *et al.* in 1975. With perfluorocarboxylate complexes $[M(OCOR_F)_2(CO)(PPh_3)_2]$ (M = Ru, Os; $R_F = CF_3$, C_2F_5 or C_6F_5) as catalysts and an acid as proton source a homogeneous catalytic system for the dehydrogenation of primary and secondary alcohols to aldehydes and ketones was developed.[87] With low catalyst loadings of complex **13** (0.03 mol%) (Scheme 13) and an excess of trifluoroacetic acid, an initial turnover frequency (TOF) of 8172 h^{-1} was achieved for benzyl alcohol (converted to benzaldehyde), while inferior TOFs were reached for secondary alcohols (529 h^{-1} for cyclohexanol). A comparison of relative efficiencies shows that Ru(II) complexes are more active than Os(II) and that carboxylates with enhanced fugitive properties increase the catalytic activity ($CF_3 > C_2F_5 > C_6F_5$). Initial coordination of a molecule of alcohol as entry into the catalytic cycle is likely and is indicated by the isolation of the stable adduct

$[Ru(OCOCF_3)_2(CH_3OH)(CO)(PPh_3)_2]$ which is not further converted. The coordinated ROH molecule is internally deprotonated by the coordinated carboxylate ligand under liberation of the free acid. The formed alkoxide complex would subsequently undergo a β-hydride elimination to form an aldehyde (or ketone) and the hydride species $[MH(OCOR_F)(CO)(PPh_3)_2]$. Reaction with the acid leads to H_2 formation and closes the catalytic cycle with regeneration of $[M(OCOR_F)_2(CO)(PPh_3)_2]$ (M = Ru, Os). Methanol as substrate is not dehydrogenated which is attributed to the slightly stronger α-CH bond in methyl groups when compared to alkyl groups present in higher primary or secondary alcohols. The original Robinson complex was also tested as catalyst for dehydrogenation of alcohols and immobilized on a polystyrene support by Ziolkowski.[88] Under comparable reaction conditions, the former authors reported activities that were 6 times higher than those determined by the latter group for secondary alcohols and, primary alcohols were poorly converted*.* Catalytic activities for secondary alcohols with TOF values up 250 h^{-1} (cyclohexanol) were obtained by Garrou *et al.* who used the complex **14** with a chelating diphosphine instead of the monodentate PPh_3 ligands in the Robinson complex.[89] The major drawback of these catalytic systems is that they do not show high turnover numbers for primary alcohols as they become deactivated by decarbonylation reactions.

Cole-Hamilton *et al.* demonstrated that simple alcohols can be dehydrogenated by using the complex $[RuH_2(N_2)(PPh_3)_3]$ (**15**) and an excess of base. The dehydrogenation of primary and secondary alcohols produced reasonable rates of hydrogen gas (up to TOF = 150 h^{-1} for EtOH). High temperatures and continuous removal of the generated hydrogen in order to make the reaction irreversible and suppress the hydrogenation of the carbonyl products were required. The Ru catalysts showed significantly increased activity when irradiated with visible light and with EtOH as substrate a TOF = 210 h^{-1} was achieved. As previously mentioned for the Robinson catalyst, decarbonylation of the aldehyde products can result in catalyst poisoning by formation of stable and catalytically inactive Ru carbonyl complexes. Irradiation with light may promote the release of CO and regeneration of the active species.[90] A mechanism in which the Ru center in the various catalytically active intermediates remains coordinated to all three PPh_3 ligands was initially proposed[90b] while later studies indicated that the active catalyst is generated in a pre-equilibrium involving PPh_3 dissociation.[90d] Bühl *et al.* inspected computationally four different reaction pathways for alcohol dehydrogenation promoted by the Cole-Hamilton catalyst precursor $[RuH_2(N_2)(PPh_3)_3]$ which is assumed to convert to the hydrogen complex $[RuH_2(H_2)(PPh_3)_3]$ as active species. In all of them, the rate determining step for hydrogen evolution was found to be the β-hydrogen elimination from a methanol or methoxide complex. The different reaction channels differ by various ligand dissociations (PPh_3 or H_2) prior to β-hydrogen elimination. Remarkably, it was found that all pathways are competitive with respect to their energy profile.[90e] Note that the role of base was not and is difficult to assess in this computational study. But the addition of base is clearly necessary to achieve an efficient turn over although also undesired side reactions like decarbonylation and aldol condensations are observed.

Beller *et al.* have screened a vast variety of Ru precursor complexes in combination with phosphine or amine ligands for the *in situ* generation of active alcohol dehydrogenation catalysts. Simple mixing of [{RuCl$_2$(*p*-cymene)}$_2$] **16** with tetramethylethylene diamine (TMEDA) (**L16**) leads to a catalytic system which shows a remarkable high turnover frequency (TOF > 500 h^{-1}) for the dehydrogenation of 2-propanol. The reaction requires a reaction time up to 11 days and the scope of substrates is limited. The unprecedented stability of this catalytic system (>250 h) indicates that di- or polyamine chelates may have a high potential as steering ligands for future investigations.[91] As will be shown below, a compendium of ruthenium complexes bearing non-innocent pincer ligands (PNPs and PNNs) have proven to be very efficient in the dehydrogenation of alcohol substrates. The structurally simple aliphatic PNP ligand **L17** cooperates with the Ru centre and during the catalytic dehydrogenation of secondary alcohols a metal-amide N(sp^2)/metal-amine N(sp^3) interconversion takes place.[92] By combining the Ru precursor **17** and an aliphatic PNN pincer-ligand **L17** shown in Scheme 13, Beller *et al.* found a highly efficient catalytic system for the clean dehydrogenation of neat 2-propanol to acetone under neutral conditions at 90 °C with an initial TOF of 8382 h^{-1} (after 2 h reaction time).[93] To date, only very few complexes showed a higher activity (see next section).



Scheme 13. Ru-complexes as homogeneous catalysts for the thermal dehydrogenation of primary and secondary alcohols to aldehydes and ketones

Milstein *et al.* reported that Ru(II) complexes with an electron-donating *t*BuPNP pincer ligand [PNP= 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine] catalyzed the dehydrogenation of secondary alcohols to ketones. A fourfold excess of base with respect to the catalyst was necessary in order to achieve high conversions and selectivity to the corresponding ketone. While higher concentration of base was detrimental for the selectivity, lower concentrations resulted in reaction inhibition.[94] A dinuclear $[Ru_2(Cl)_4(\mu_2\text{-}\kappa^2\text{-}N_2)(PNN)_2]$ complex **19** based on a hemilabile PNN pincer ligand [PNN= 2(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine], showed higher efficiency after activation with 4 equivalents of base (NaO*i*Pr).[95] The electron-rich PNP- and PNN-ruthenium(II) pincer complexes which contain a BH_4^- ligand in the coordination sphere of the metal, [RuH(BH_4)(*t*Bu-PNP)] (**20**) and [RuH(BH_4)(*t*Bu-PNN)] (**21**), showed improved TOFs of 11 - 19 h^{-1} in the dehydrogenation of

2-propanol. The catalytic activity of the PNN ruthenium complex is slightly higher than the complex bearing a PNP pincer ligand, which was taken as an indication of the “hemilabile” NEt_2 amino group, which is a coordination and de-coordination within the catalytic cycle.[96]

As mentioned above, the efficient dehydrogenation of primary alcohols to aldehydes is a challenging transformation. The catalytic systems based on the discussed Ru complexes show the tendency to further decarbonylate the aldehydes or to promote the dehydrogenative coupling reaction whereby primary alcohols are converted to their corresponding esters (Tishchenko type reaction; see following section).

Dehydrogenation of alcohols to esters or acids

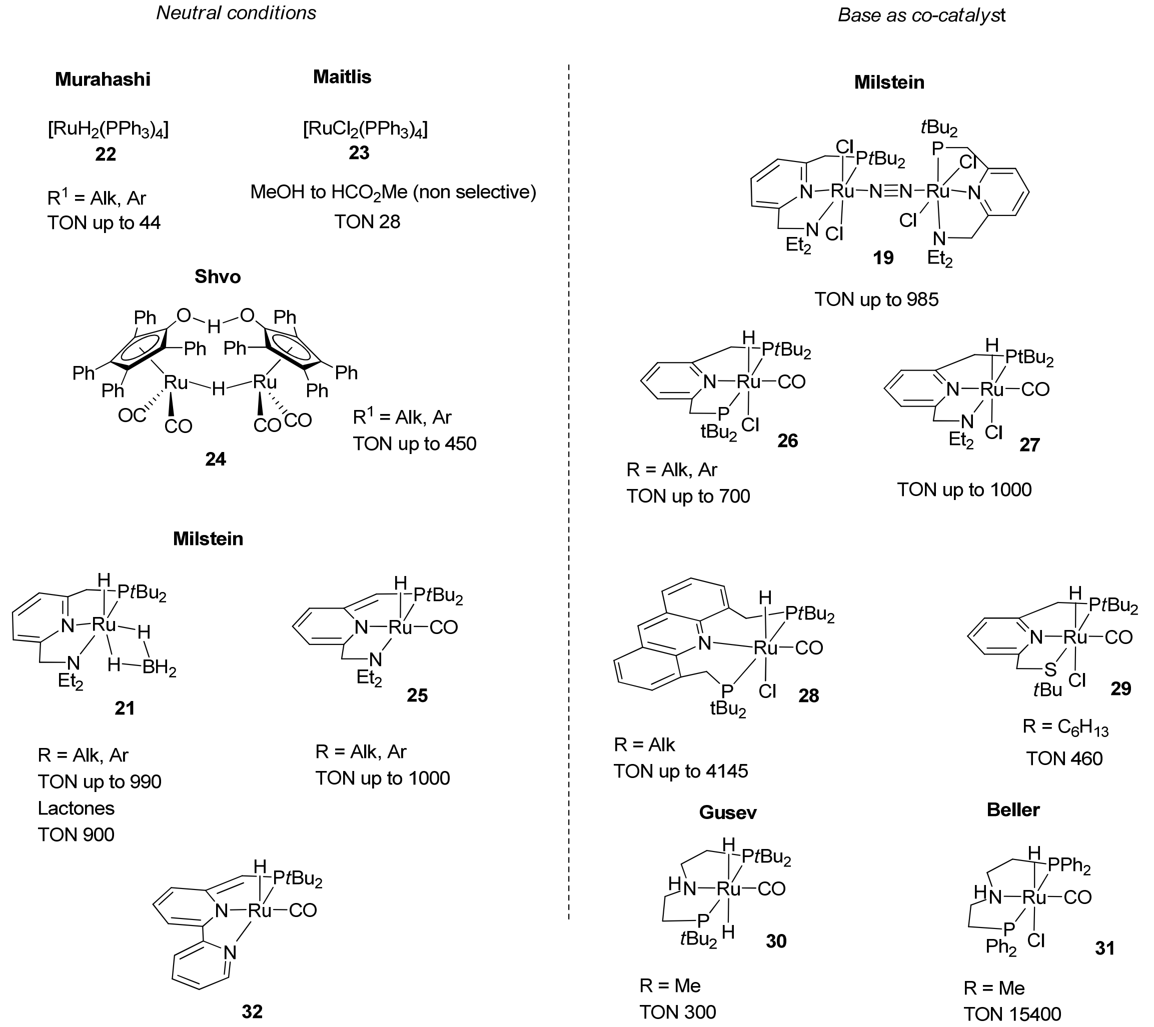
The direct conversion of alcohols into carboxylic acid derivatives, without the need of a sacrificial oxidant and the only production of H_2 as by-product is a remarkable example of an atom economic process. With alcohols available from biomass as feedstock such a process opens up a realistic environmentally friendly alternative to conventional alcohol oxidations. Before the pioneering work of Murahashi and Shvo, the catalytic dehydrogenation of two equivalents of a primary alcohol to the corresponding “symmetric” ester under evolution of H_2 ($2\ R\text{-}CH_2\text{-}OH \rightarrow R\text{-}CO\text{-}O\text{-}CH_2\text{-}R + 2\ H_2$) was limited to few non-selective heterogeneous systems. Murahashi *et al.* reported the successful transformation of primary alcohols to esters (Scheme 14 A) and of diols to lactones (Scheme 14 B) with $[RuH_2(PPh_3)_4]$ (**22**) as catalyst.[97] Independently, Shvo *et al.* demonstrated that $[(\eta^4\text{-}tetracyclone)(CO)_3Ru]$[98] and a related dimeric complex **24** were effective pre-catalysts for the direct oxidation of benzyl alcohol to benzyl benzoate, omitting the use of an hydrogen acceptor and insinuating the cooperativity of the cylopentadienone ligand in the catalytic cycle.[99] The concept of metal-ligand cooperativity in dehydrogenative processes has been developed extensively in the recent years, especially for dehydrogenation and reversible hydrogenation processes.[21] Considerably more efficient catalysts were developed by Milstein *et al.* and others with the previously mentioned ruthenium pincer complexes shown in Scheme 13. Ruthenium(II) hydride complexes bearing PNP (**26**) or PNN ligands (**19**, **27**) catalyzed the direct dehydrogenation of two equivalents of alcohols to esters (dehydrogenative coupling reaction, DHC). The reversible aromatization/dearomatization of the central N-heterocycle of the ligand and the hemilability of the amino group were proposed as key-features of a novel dehydrogenation mechanism.

Eq. 25 $RCH_2OH \longrightarrow RCH{=}O + H_2$

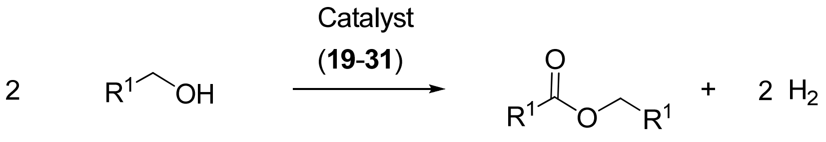
Eq. 26 $RCH{=}O + RCH_2OH \longrightarrow RCH(OH)(OCH_2R)$

Eq. 27 $RCH(OH)(OCH_2R) \longrightarrow RCO_2CH_2R + H_2$

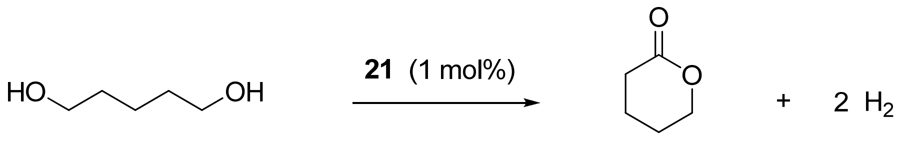
Catalysts



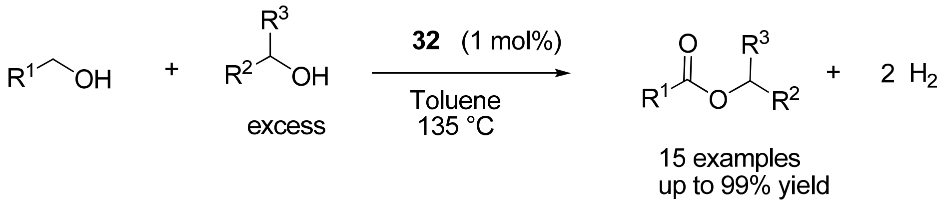
A) Homocoupling of alcohols



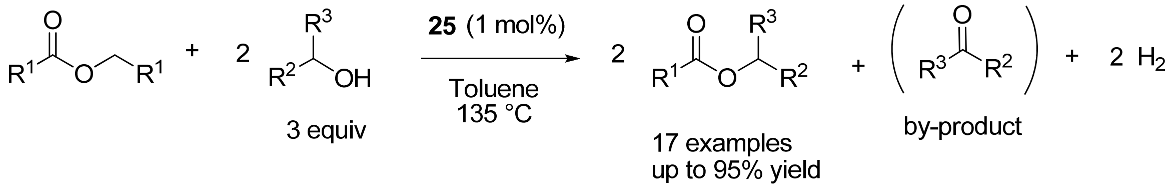
B) Intramolecular coupling of diols



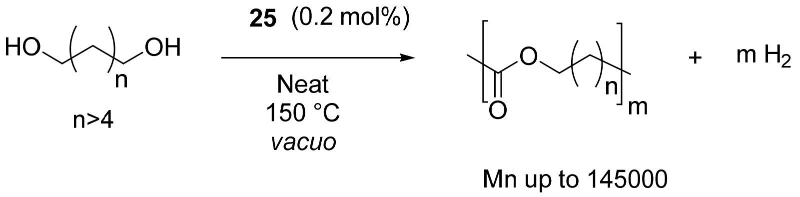
C) Cross-Coupling of primary and secondary alcohols



D) Dehydrogenative transesterification



E) Polydehydrogenative coupling of diols



Scheme 14. Active Ru-catalysts for the conversion of alcohols to esters and H_2 according to equations A-E)

While these complexes require basic conditions in order to achieve respectable turn over numbers, the most efficient catalyst [RuH(CO)(PNN-H)] (**25**) operates under neutral conditions and is obtained by deprotonation of the PNN ligand and concomitant chloride elimination from [RuH(Cl)(CO)(PNN)] (**27**). The catalytic activities of the hydrido borohydride Ru(II) pincer complex **21** was also tested with a series of primary alcohols and diols. Esters and lactones, respectively, were obtained as products (see Scheme 12 B), with TONs up to 1000 (esters) and 900 (lactones). The complexes do not disproportionate pure benzaldehyde to benzyl benzoate which leads to the following mechanistic proposal including three general reaction steps: dehydrogenation of the alcohol to the aldehyde (Eq. 25), hemiacetal formation from the aldehyde and unreacted alcohol (Eq. 26) and dehydrogenation of the hemiacetal to the corresponding ester (Eq. 27). It is likely, that these steps are involved in all the reactions shown in Scheme 14, that is homo-coupling (A), intramolecular coupling (B), cross-coupling (C), dehydrogenative transesterification (D), and dehydrogenative polymerisations (E).[100] The NEt_2 amino group in the Milstein complex was replaced by a thioether group resulting in a PNS ligand. Although the thioether "arm" of the PNS complex **29** was expected to be hemilabile, the ligand lacks the ability to serve as an internal base and consequently little selectivity and efficiency was observed with this catalyst.[101]

Following the dearomatization/aromatization concept as a key-feature of a successful ligand in the catalytic dehydrogenation of alcohols, an acridine-based ruthenium pincer complex [RuHCl(CO)(A-*i*Pr-PNP)] (**28**) [(A-*i*Pr-PNP) = 4,5-bis-(diisopropylphosphinomethyl)acridine] was prepared. In the presence of catalytic amounts of base (1 equiv of KOH relative to Ru) a high yield of hexyl hexanoate was obtained from 1-hexanol with TON 4145. The reaction could be controlled to give selectively hexyl acetal under base free conditions (TON 3575).[102]

The dehydrogenation of ethanol to the symmetric ester and H_2 is of particular interest because ethyl acetate (AcOEt) is a widely used industrial bulk chemical. This reaction was extensively studied using heterogeneous catalysts under acceptorless conditions.[103] Milstein's Ru based catalytic system is able to promote the effective dehydrogenation of primary and secondary alcohols but only limited activity has been observed with ethanol as substrate. Gusev *et al.* studied the steric and electronic factors of the pincer backbone that influence the catalytic activity[104] and via extensive screening of known pincer complexes, an optimized catalyst was found for this transformation.[105] With low catalyst loadings of [RuClH(*H*PNP^{Ph})(CO)] (**31**) [*H*PNP^{Ph} = bis-(2-diphenylphosphinoethyl)amine] in the presence of base, high yields of the ester AcOEt were obtained with a TON of 15400. The addition of precise amounts of base is essential so that under these conditions the most efficient catalytic system for the homogeneously catalyzed dehydrogenation of alcohols is reached.

Cross-dehydrogenative coupling of primary and secondary alcohols (Scheme 14C) has been accomplished using a ruthenium bipyridine pincer complex under neutral conditions by taking advantage of the diminished reactivity of secondary alcohols to undergo dehydrogenation.[106, 107] The symmetric esterification from primary alcohols was only observed as a minor side reaction.

An interesting example of an atom economic process is the dehydrogenative transesterfication reaction outlined in Scheme 14D. When symmetrical esters are reacted with an excess of a secondary alcohol, unsymmetrical esters are obtained as products under the release of two equivalents of hydrogen. Ketones from the secondary alcohols are obtained as by-product.[108] The process is efficiently catalyzed by de-aromatized complex **25** without the need of any additive. Upon transesterification, the released primary alcohol undergoes dehydrogenative coupling with a second equivalent of the secondary alcohol to give an additional equivalent of the unsymmetrical ester.

Typically polyesters are synthesized using a step-by-step polycondensation reaction. This classical simple method tolerates a broad range of substrates but is limited by the low molecular weights of the resulting polymers. Established procedures use the condensation of diacids and diols and at temperatures of about 250 °C, reduced pressure and with Lewis-acids as promoters give polymers in the range M_w 5000 to 10000. Furthermore, the presence of by-products that are retained in the polymer matrix influence the properties of the final polymer. More defined polymer properties are obtained in ring opening polymerization (ROP) of cyclic monomers but here the process is confined by the availability of cyclic monomers. Under these aspects, the polydehydrogenative coupling (see Scheme 14E) of diols with liberation of H_2 offers an attractive alternative because a wide range of diol substrates is available and the process is highly atom economic. The dearomatized [RuH(CO)(PNN)] complex **25** served as efficient catalyst in the dehydrogenative polymerization of α,ω–diols to generate polyesters. The gaseous hydrogen produced was continuously removed under vacuum to drive the equilibrium towards the product side, resulting in the formation of a high molecular weight polymer (M_n up to 145000 g/mol) and moderately narrow PDI values 2 - 3.[100c] To date, this method can only be applied in the polymerization of diols in which the hydroxyl groups are separated by at least six carbons. Diols with fewer carbons between the hydroxyl functions undergo cyclization to lactones with 1,5-pentanediol as bifurcation point which under dehydrogenation leads to a mixture of polyester and lactone in a ratio of about 1 : 2.

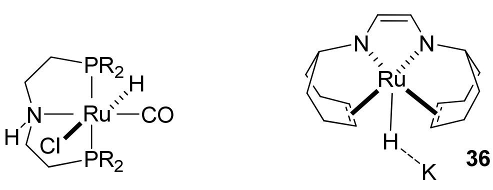
Most of the oxidations of alcohols to acids proceed by using stoichiometric amounts of toxic oxidizing agents or the use of pressurized dioxygen. A recent report demonstrated that complex **25** served as catalyst for the conversion of primary alcohols to carboxylic acids in one-step with water as terminal oxidant and the reaction proceeded with liberation of two molecules of H_2.[109] This represents the first example of an efficient metal based catalyst that operates in water and drives this reaction without the addition of a further oxidant.

Ruthenium-based homogeneous catalysts for the production of hydrogen from methanol have been investigated in the past years but they show little activity and selectivity. Most of the reactions unselectively afforded carbon-containing by-products: formaldehyde,[110] methyl formate (Scheme 14B),[111] formate salts,[112] or acetic acid.[113] The groups of Beller[114] and Grützmacher[115] described recently the first efficient aqueous-phase methanol dehydrogenation process, catalyzed in both cases by well-defined ruthenium complexes (**33** and **36**) bearing cooperative ligands. As mentioned in the introduction, this approach may establish the starting point for the development of methanol as hydrogen storage "material" since the reaction temperatures in both examples lie significantly below 100 °C. At ambient pressure almost the complete 3 equivalents of H_2 are released from the H_3COH/H_2O mixture allowing the direct use of methanol in PEM fuel cells.[116]

The catalytic cycle for methanol dehydrogenation shown in Scheme 15A was developed by Beller *et al.* based on of the known properties of complexes [RuClH(HPNP^{Ph})(CO)] (**30** and **31**) in the dehydrogenation of secondary alcohols to ketones or EtOH to AcOEt which was reported by the same authors and Gusev *et al.*[92, 105, 106] As in the dehydrogenation of higher primary or secondary alcohols, addition of base is essential to remove HCl from the pre-catalyst **33** and generate the bifunctional [Ru(II)PNP] active species **34.** The authors propose the activation of a methanol molecule which binds with the acidic protic OH group to the amide function of the catalyst and the (weakly) hydridic α-CH group to the Ru centre (see **TS-A** in Scheme 15). This interaction triggers the liberation of a hydrogen molecule and transient generation of formaldehyde ($H_2C{=}O$) which is further converted under aqueous alkaline conditions to $H_2C(OH)_2$ a direct precursor of formate (HCO_2^-) after losing a second molecule of hydrogen. Decomposition of formate to CO_2 and a third hydrogen molecule regenerates the active form of the catalyst (Scheme 15A). Very high TONs of 350000 were reported using this catalytic system. A very similar reaction sequence was established in the dehydrogenation reaction with the Grützmacher catalyst [K(dme)$_2$][RuH(trop$_2$dad)] (**36**). This complex contains the chemically and redox *non-innocent* diolefin diazadiene ligand trop$_2$dad which participates actively in the alcohol dehydrogenation. The methanol molecule is added across the Ru-N bond and thereby a methoxide group is bound to the metal centre. Activation of the α-C-H bond of the coordinated methoxide occurs and a hydride (H^-) is transferred to the diazadiene-backbone of the ligand (see **TS-B** in Scheme 15) which is fully hydrogenated from a trop$_2$dad ligand to a bis(amino)ethylene ligand (trop$_2$dae). This process is further accompanied by a reduction of the Ru(II) centre to Ru(0) (see Scheme 15B). Model reactions indicate that in this catalytic process, methanol is first dehydrogenated to formaldehyde: $MeOH \rightarrow H_2C{=}O + H_2$, which - likely still coordinated to the metal centre and thereby activated - reacts rapidly with water to form di(hydroxy)methane: $H_2C{=}O + H_2O \rightarrow H_2C(OH)_2$. This is again catalytically dehydrogenated to formic acid: $H_2C(OH)_2 \rightarrow HCOOH + H_2$, which is finally converted to CO_2 and H_2, with the highest TOF reported to date for the decomposition of pure formic acid (24000 h^{-1}). The dehydrogenation of aqueous methanol proceeds best under slightly basic conditions which are needed to promote the dehydrogenation of the isolated complex **37** to the active hydride complex **36** and to sequestrate the released CO_2 as carbonate.

$$MeOH + H_2O \xrightarrow{\text{Catalyst}} CO_2 + 3\ H_2$$

Beller **Grützmacher**

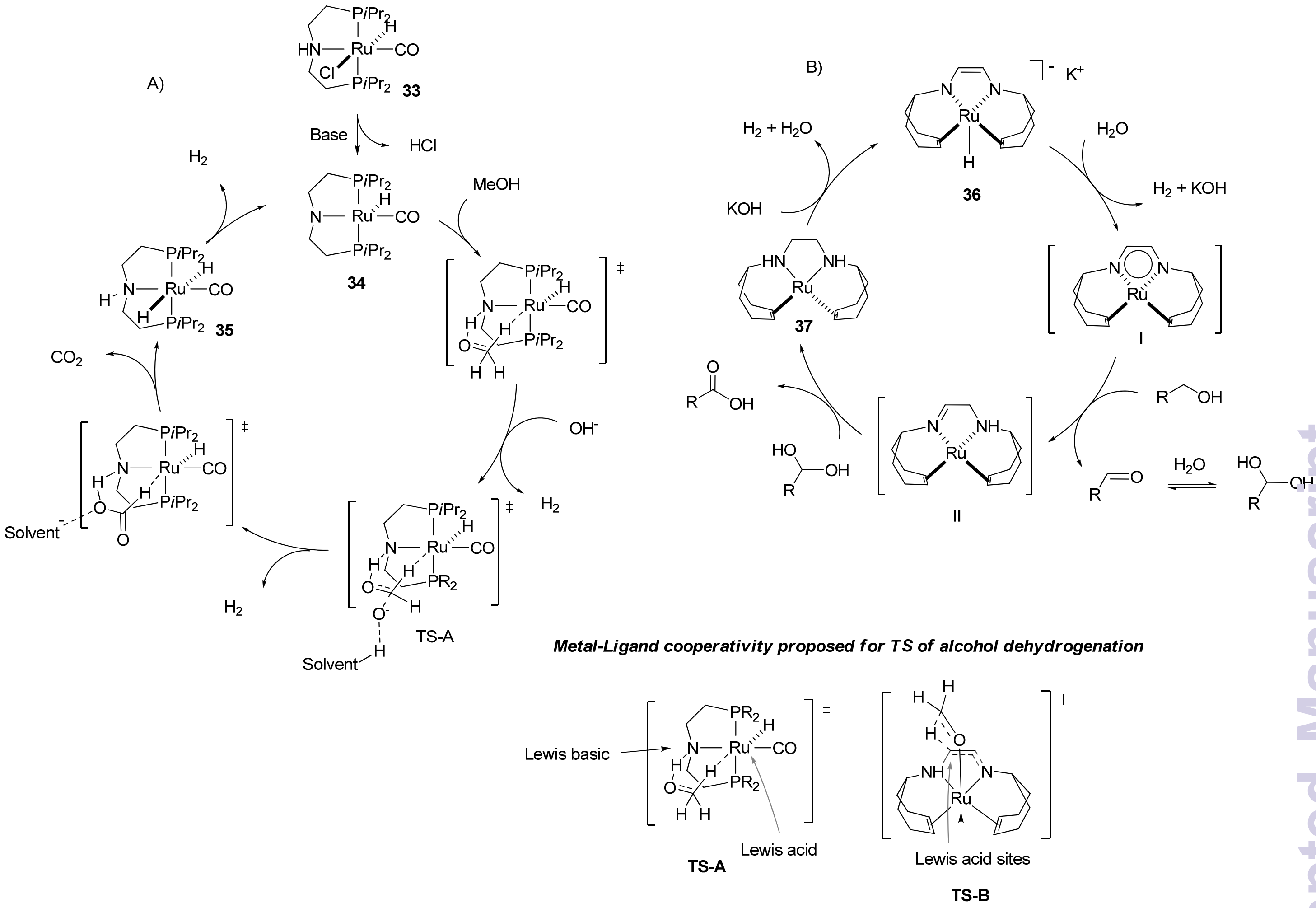


36

	TOF (3h)
R = Ph (**31**)	1093 h^{-1}
*i*Pr (**33**)	2670 h^{-1}

TOF 24000 h^{-1} conversion of HCO_2H to CO_2/H_2

TOF (10 h) 16 h^{-1} conversion MeOH to CO_2

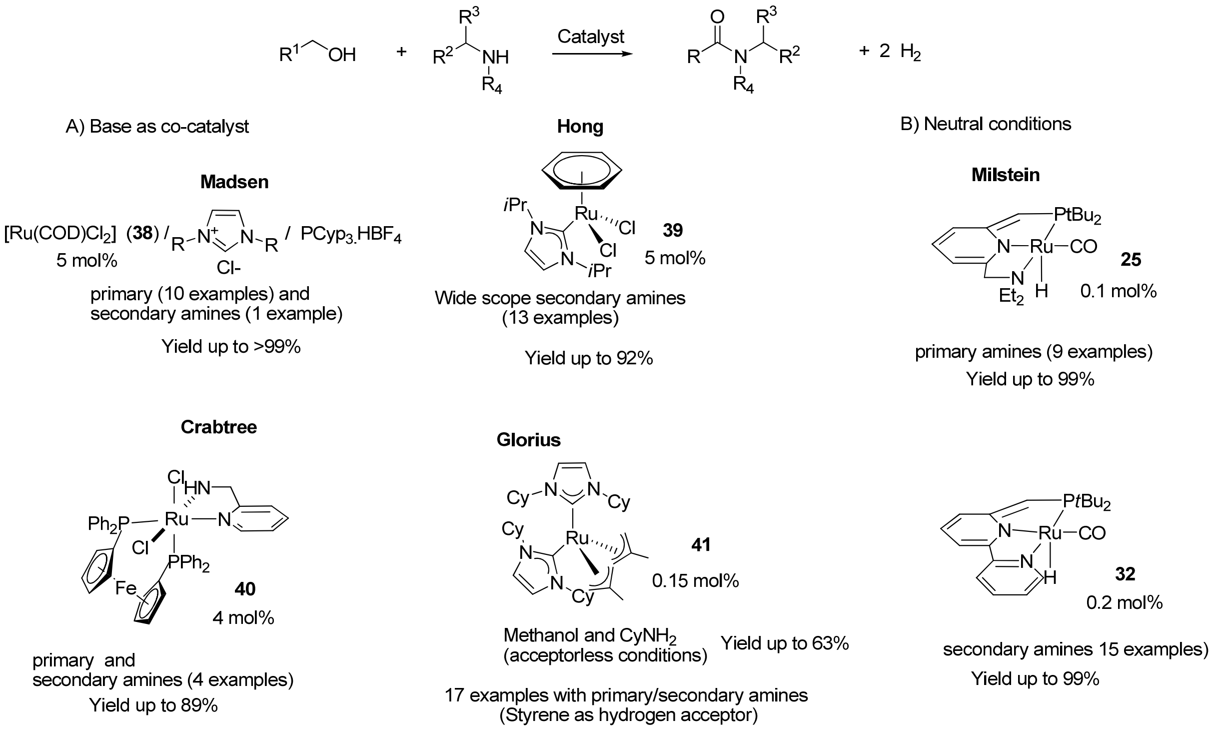


Scheme 15. Catalyzed sequential decomposition of MeOH/H_2O to CO_2/ $3H_2$ and proposed catalytic cycles for aqueous phase methanol dehydrogenation by Beller and Grützmacher catalysts.

Bimolecular dehydrogenation of alcohols and amines to amides

The amide group is one of the most common functional groups needed in the synthesis of pharmaceutically active compounds.[117] New chemical reactions leading to amide formation are investigated in order to overcome the limitations associated with the need of stoichiometric oxidants or pre-functionalized substrates. Amide bond formation using enzymatic catalysis solves some of these issues, but the narrow substrate specificity of the currently available enzymes limits their practical use. A new reaction for amide formation that may contribute to circumvent these problems is the catalyzed dehydrogenative (intra or intermolecular) coupling of primary alcohols with amines under liberation of H_2.

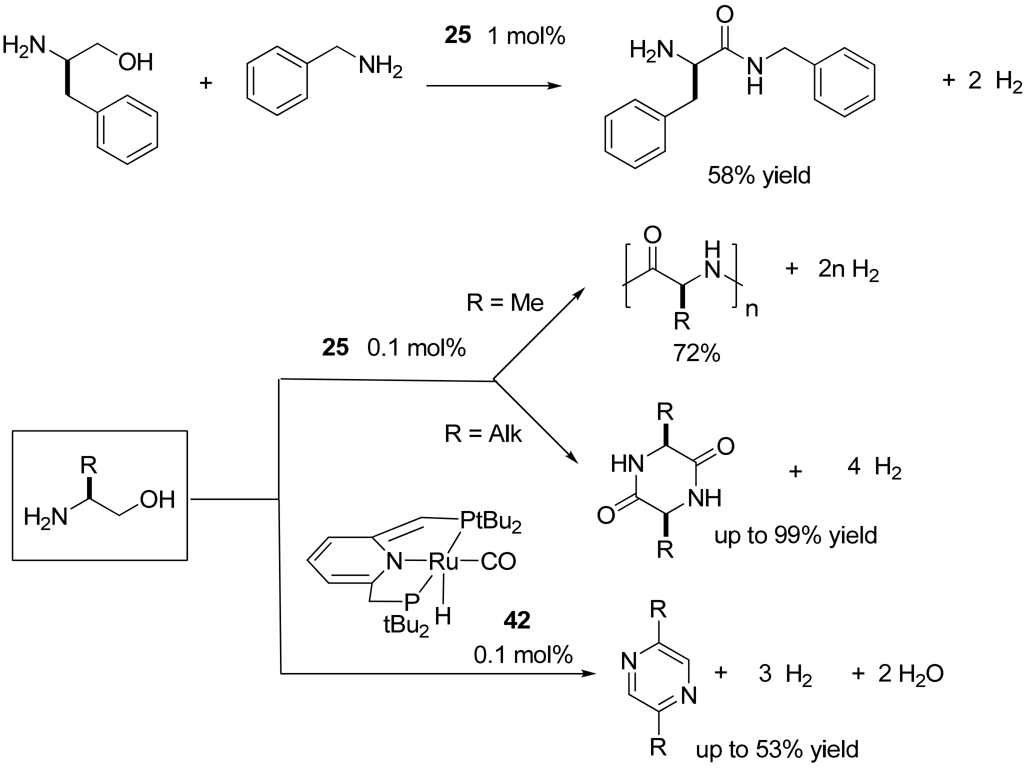
A number of homogeneous catalytic systems have been reported based on Ru complexes with pyridine pincer, carbene or phosphine ligands. Selected examples are given in Scheme 16. The dearomatized Ru-PNN complex **25** catalyses efficiently the transformation of equivalent amounts of alcohols and amines under neutral conditions (TON 1000).[118] Likely the mechanism involves the three general steps (a) dehydrogenation of the primary alcohol to an intermediate aldehyde; (b) reaction with the amine to form a hemiaminal and (c) hemiaminal dehydrogenation to give the amide product, similar to the Eq. 25-27 in case of dehydrogenative coupling of alcohols. When amines of low nucleophilicity (e.g. an aniline derivative) are used, the alcohol competes with the amine in the reaction with the aldehyde and esters are formed as side-products. The reactions selectively convert primary amines while secondary amines such as dibenzylamine do not react. The amidation reactions are sensitive to steric hindrance at the α positions of either the alcohol or the amine. For example the use of sterically hindered 2-methyl-1-butanol and 2-methylhexamine resulted in much lower yields of amides. One further competing reaction is the elimination of water from the hemiaminal to form an imine. This transformation can be influenced by a careful selection of the pincer ligand (see next section).[119] The same authors presented recently an example of a catalyst that allows the synthesis of amides from secondary amines using a Ru(II)PNN pincer type catalyst (**32**) containing a bipyridine derivative as ligand. TONs up to 2750 were obtained in the conversion of secondary amines to tertiary amides.[120] Madsen *el at.* reported the *in situ* formation of a Ru carbene complex which can also catalyze the dehydrogenative cross coupling of alcohols and amines, although the protocol requires higher catalyst loadings (5 mol%) and the need for rather large, sub-stoichiometric amounts of base.[121] Hong *et al.* introduced the well-defined N-heterocyclic carbene ruthenium complex **39** that catalyzed efficiently the direct amide synthesis from alcohols using secondary amines.[122] Another prominent example reported by Crabtree *et al.* features the easily tunable amidation catalyst (**40**) which is assessed with aminopyridine and diphosphine chelate ligands. This class of complexes is well known as catalysts for hydrogenation and transfer dehydrogenation reactions and in consequence, based on the principle of microscopic reversibility, catalytic activity can be expected for the reverse process that is dehydrogenation. After an extensive catalyst screening, the authors concluded that the presence of an N-H group in the ligand is essential for the activity of the catalyst and presumed that hydrogen bonding with the substrate favours the hydrogen release.[123] Glorious *et al.* reported the dehydrogenative coupling of primary and secondary amines with methanol to generate formamides promoted by the biscarbene ruthenium complex **41** as pre-catalyst. The reaction is limited to one example under acceptorless conditions and shows moderate yields. With styrene as hydrogen acceptor, however, a quantitative conversion of methanol was achieved.[124]



Scheme 16. Ru based catalytic system for the one-pot dehydrogenation alcohols and amines to amides

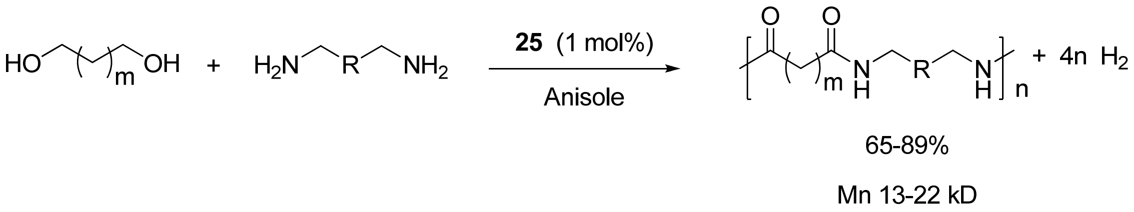
Note in this context, that alcohols and amines can be very efficiently coupled (TOF > 10000 h^{-1}; TONs > 10000) using sacrificial hydrogen acceptors and catalyst based on the concept of metal-ligand cooperativity.[125]

By using the dearomatized Ru(II)(PNN) pincer complex **25**, dehydrogenative coupling of chiral β-amino alcohols with an amine gave β-hydroxy amides under retention of the configuration and liberation of H_2. In the absence of an external amine, intramolecular-dehydrogenative coupling reactions of β-amino alcohols lead to the formation of cyclic or linear peptides. The selectivity of the reaction catalyzed by **25** is strongly influenced by the steric demand of the substituents in the substrate. Large substituents in α-position to the amino group lead to the formation of the corresponding cyclic dipeptides. On the contrary, when (*S*)-(+)-2-amino-1-propanol is used as substrate, good yields of polyalanine (73%) are obtained in the dehydrogenation reaction. Hence, this protocol may be indeed developed into a convenient alternative method to traditional peptide syntheses. The dearomatized Ru(II)(PNP) complex **42** leads, on the other hand, to a sequential dehydrogenative coupling and dehydration of a β-aminoalcohols to pyrazines (Scheme 17).



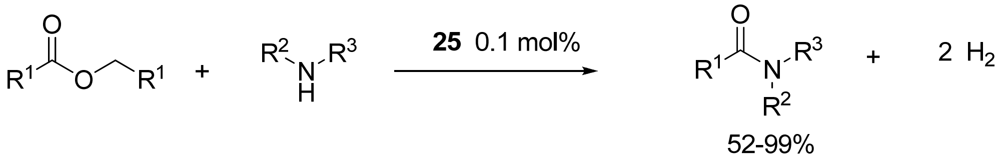
Scheme 17. Ru-catalyzed dehydrogenative coupling of β-aminoalcohols to amides, peptides and pyrazines

Polyamides, such as nylon and related structures are highly relevant macromolecules and widely used materials. Consequently, any synthetic method giving polyamides and tolerating functional groups is welcome and the dehydrogenative coupling between polyols and polyamines under elimination of hydrogen may be just such a method. Guan and Milstein demonstrated independently that the direct polyamidation reaction using low catalyst loadings of the dearomatized Ru-PNN complex **25** (1 mol%) is feasible (Scheme 18). In an optimization procedure, anisol was identified as polar solvent for the especially efficient polymerization leading to polyamides with M_n > 13 kD. With the addition of dimethyl sulfoxide (DMSO) the molecular weight was improved to M_n > 22 kD. The reaction shows very high selectivity for amide formation and polyesters were not detected. This atom economic process could become valuable for a low cost production of polyamides applicable in biomaterials under avoidance of waste.[126]



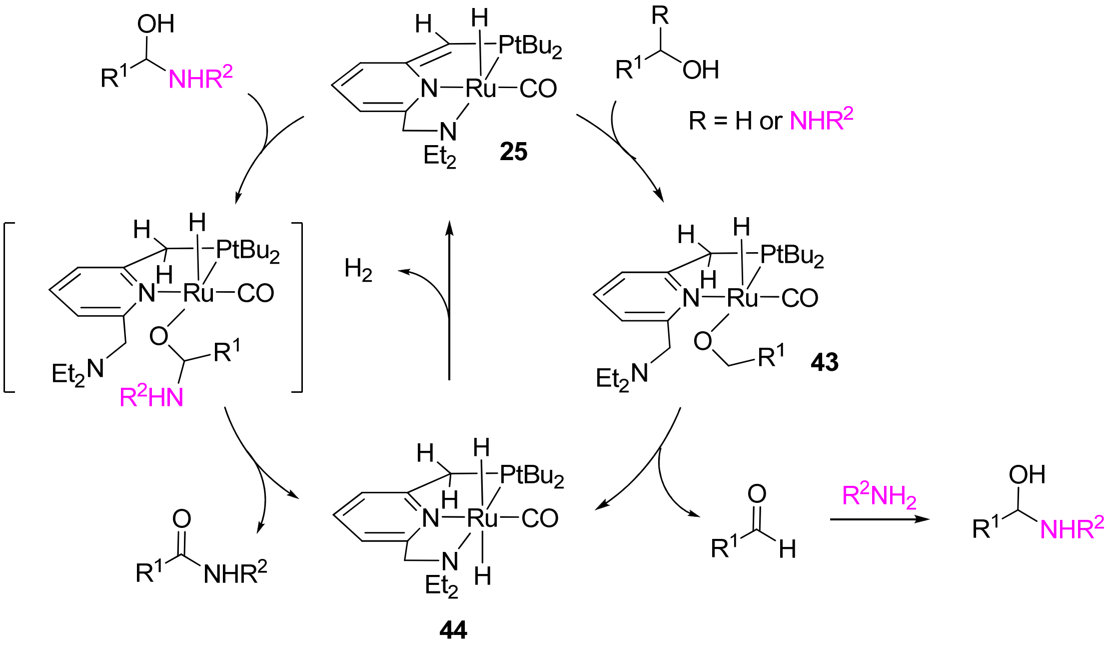
Scheme 18. Dehydrogenative coupling diols and diamines to polyamides

Similar to the alcohol acylation process, the acylation of amines with liberation of two equivalents of H_2 has been likewise achieved with Ru(II)(PNN)-type complexes (Scheme 19). The coordination of both the ester and the amine to the Ru centre followed by intramolecular nucleophilic attack of the pre-activated N-H of the amine on the acyl functionality is proposed as key-step in the mechanism. This reaction proceeds smoothly with ethyl acetate as convenient acetylating agent of amines.



Scheme 19. Dehydrogenative coupling of esters and amines to amides

Details of the proposed reaction mechanism for the Ru-PNN catalyzed amidation have been investigated using density functional theory calculations.[127] It has been proposed that initial dehydrogenation of the alcohol occurs by proton transfer to the backbone of the ligand. Pyridine aromatization and formation of the alkoxide Ru complex (**43**) are the result of this process. Experiments al low temperature (-80 °C) demonstrated that the addition of alcohols to the dearomatized complex **25** resulted in the reversible formation of an alkoxide complex. When the reaction mixture containing the intermediate was warmed to -30 °C, alcohol dehydrogenation occurred and formation of the *trans*-hydride complex (**44**) was observed. However no free aldehyde was detected, which was reversibly trapped between the metal centre and the methine carbon of the side arm of the ligand forming a new complex. These findings implied that a typical alkoxide β-hydride elimination may not account for the alcohol dehydrogenation in this case, as it will require an open coordination site in *cis*-position and the CO or PNN ligands are not labile at low temperatures. Another possibility supported by the latest calculations involves direct "*krypto*"-(H^+,H^-)-hydrogen transfer from the alcohol to the side arm of the ligand and the metal centre reminiscent to Noyori's bifunctional mechanism.[128] In the next step, elimination of dihydrogen from complex **44** would regenerate the active catalyst. The second dehydrogenation of the hemiaminal as key-intermediate occurs in a very similar manner forming the amide. This prevails as product in this catalytic system relative to the formation of the imine (Scheme 20).

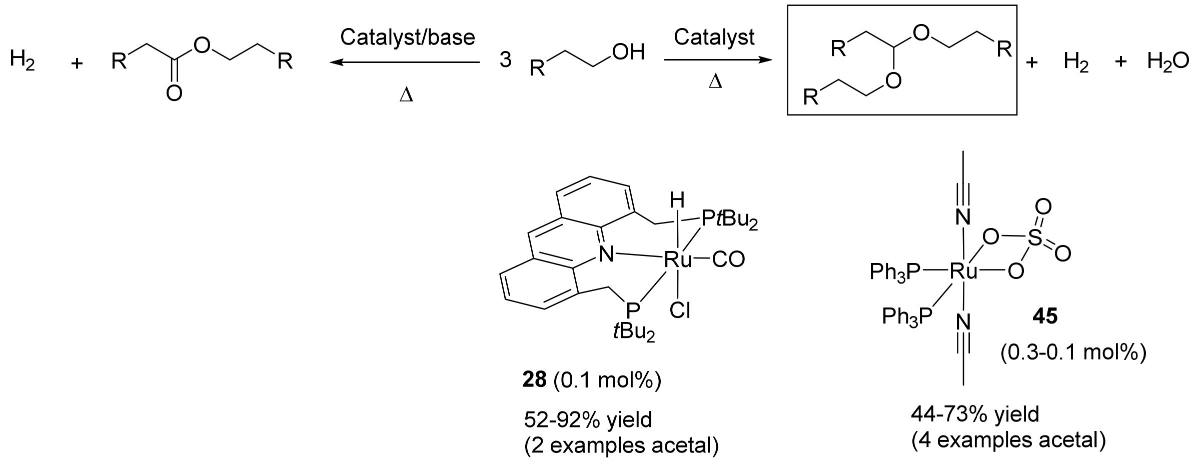


Scheme 20. Mechanism proposed on DFT computations for the dehydrogenative acylation of amines with alcohols.

Tandem dehydrogenative coupling-dehydration reactions with alcohols

Conversion of alcohols to acetals

While the pyridine pincer Ru complex **25** failed as catalyst in the conversion of alcohols to acetals, the acridine based species **28** can promote the reaction in the absence of any additive with good efficiency (yields up to 92%). However, only 1-hexanol and 1-pentanol are successfully converted to the corresponding acetals and hydrogen. When base is added, the reaction gives exclusively the symmetric ester as product. It is proposed that in contrast to the pyridine type ligand in **25**, the much longer Ru-N bond and bent central acridine ring enhances the “hemilability” of the ligand, creating a vacant coordination site. Therefore, an alcohol molecule is more readily coordinated and deprotonated by the basic site in the acridine ligand. Subsequently, β-H elimination leads to an aldehyde which reacts with a second molecule of alcohol to form a hemiacetal [see also Eq. 25 and 26]. The hydride form of the catalyst loses one equivalent of H_2 and the hemiacetal undergoes a loss of water (dehydration) to the corresponding enol ether intermediate. Finally, the addition of a third molecule of alcohol to the double C=C enol bond yields the acetal product shown in Scheme 21.[129] With the simple phosphine complex $[Ru(SO_4)(ACN)_2(PPh_3)_2]$ (**45**) as catalyst, also 1-butanol and benzyl alcohol were converted in 44 – 73% yield at even lower temperatures.[130]

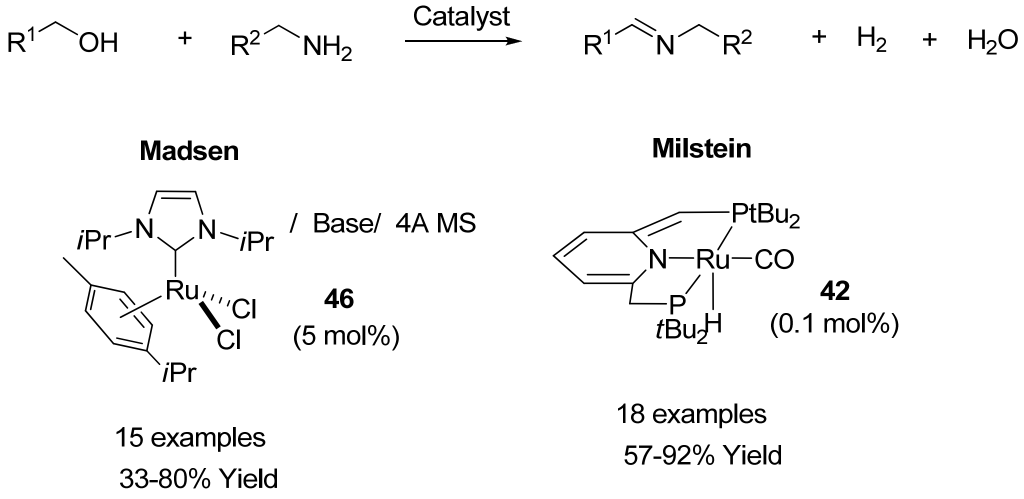


Scheme 21. Dehydrogenative coupling-dehydration of alcohols to esters or acetals catalyzed by Ru complexes

Conversion of alcohols to imines, pyrazines, or pyrroles

The Ru(II)(PNN) and Ru(II)(PNP) pincer type complexes show very different performances in catalytic dehydrogenation reactions. The complex **42** catalyzes under neutral conditions the dehydrogenative coupling of alcohols with amines leading to imines instead of amides and only one equivalent of hydrogen.[131] It has been proposed that the formation of amides *vs.* imines may require that the hemiaminal remains coordinated to the metal and is rapidly dehydrogenated to give an amide. When the hemiaminal dissociates form the metal, simple thermal dehydration to the corresponding imine occurs under the reaction conditions. In the case of Ru(PNP) complexes which lack the hemilabile amine “arm” and are sterically more encumbered, the aldehyde may dissociate more easily from the metal, form free hemiaminal in solution which then eliminate water to give the imine. DFT calculations on this catalytic system are in agreement with the observed selectivity.[132]

Following the investigation of the amidation of alcohols catalyzed by several ruthenium N-heterocyclic carbene complexes (see Scheme 16), Madsen *el al.* used a modified catalytic system which consisted of a Ru(II) arene NHC-carbene precursor complex (**46**), DABCO as base, and molecular sieves to continuously remove water during the reaction. This protocol has been applied with success for the dehydrogenative coupling of benzylic alcohols and sterically hindered primary amines as coupling partners (Scheme 22).[133] Huang *et al.* reported a modified version of pyridine based PNN and PNP pincer ligands in which the CH_2 group of the phosphine “arm” is replaced by an NH group in order to influence electronically the deprotonation and dearomatization steps. These new complexes gave interesting preliminary results in the dehydrogenative coupling of two amines to symmetric imines with the concomitant formation of H_2 and NH_3.[134]

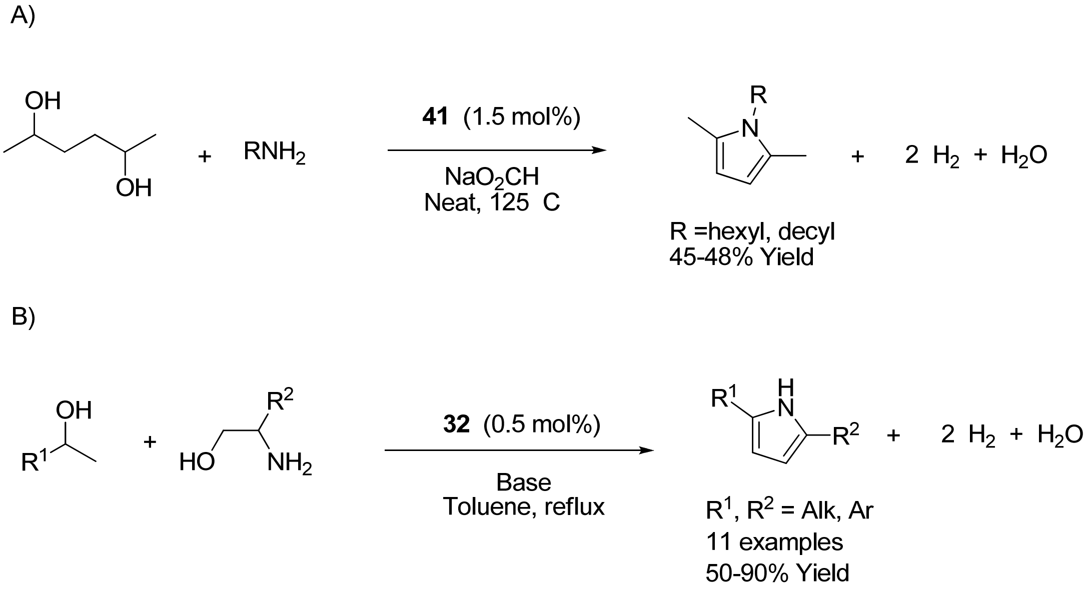


Scheme 22. Tandem dehydrogenative coupling and dehydration of alcohols to imines catalyzed by Ru complexes

As already mentioned, the combination of 1 mol% of Ru(II)(PNP) complex **26** and one equivalent of base or the direct application of a deprotonated and dearomatized Ru(II)(PNP) complex **42** leads to sequential dehydrogenative coupling and dehydration of a β-aminoalcohols to pyrazines. Given that the PNP ligand is less hemilabile, sterically more bulky, and provides no free coordination site for the amino group, one can assume that the aldehyde formed in the first dehydrogenation step dissociates more readily from the metal centre and condenses with a second equivalent of amino alcohol to form a 1,4-dihydropyrazine intermediate. This is subsequently converted in a second dehydrogenative process to give a pyrazine as final product (Scheme 17).

The catalyzed dehydrogenative version of the Paal-Knorr synthesis of pyrroles, using a 1,4-diol instead a 1,4-diketone has been investigated by Crabtree *et al.* The combination of a diphosphine aminopyridine Ru(II) complex (**41**) and sodium formate promoted the dehydrogenation of 2,5-hexanediol and condensation with a series of primary amines to the corresponding *N*-functionalized 2,5-dimethyl pyrroles which were obtained in moderate yields (up to 48%; see Scheme 23A).[124]

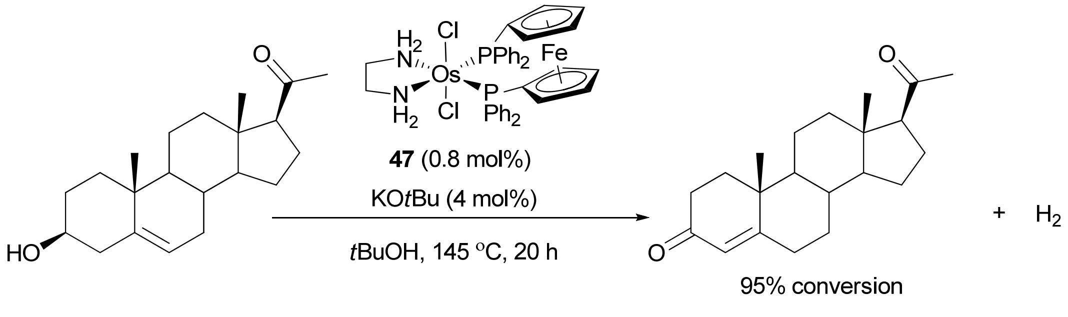
Besides the synthesis of peptides and pyrazines from β-amino alcohols under the extrusion of H_2, the catalyzed dehydrogenative coupling reaction between amino alkohols with substituents R^2 adjacent to the NH_2 group and a secondary alcohols resulted in the formation of 2,3-susbtituted pyrroles (Scheme 23B). The reaction is efficiently promoted by ruthenium complex **32** as catalysts with a phosphine bipyridine PNN pincer ligand in combination with a base.[135]



Scheme 23. Ru-promoted dehydrogenation-dehydration of alcohols and amines to pyrroles

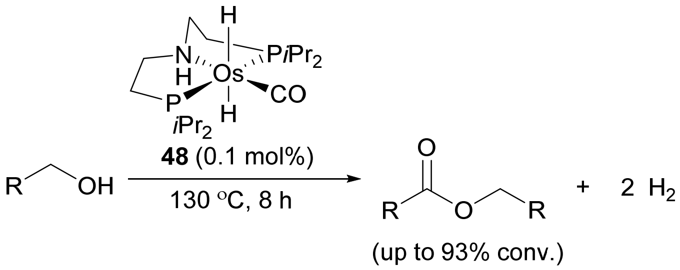
3.2.2.2 Transformations catalyzed *by Os, Rh, Ir, Co, and Re-complexes*

Besides ruthenium, recently bis(phosphine)-diamine osmium complexes have been utilized in the acceptorless dehydrogenation of alcohols. The bis(phosphine) ferrocene derived osmium complex **47** shown in Scheme 24 showed good reactivity and converted secondary alcohols to the corresponding ketones and hydrogen.[136] This complex showed especially good reactivity in the dehydrogenation of homo-allylic alcohols such as the steroidal alcohol shown below. The isomerized α,β-unsaturated ketone was obtained in nearly quantitative yield.



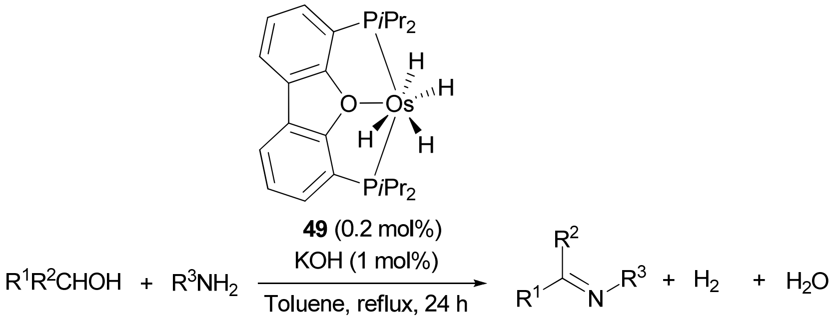
Scheme 24. Os-catalyzed dehydrogenation of homo-allylic alcohol

In 2011, Gusev *et al.* reported another type of osmium pincer-complexes bearing a PNP-ligand. These complexes were tested in various alcohol dehydrogenation reactions.[137] The osmium(II) dihydride complex **48** shown in Scheme 25 was shown to be effective in the dehydrogenative coupling of primary alcohols to afford the corresponding esters and two molecules of hydrogen were released (Tishchenko-type reaction).



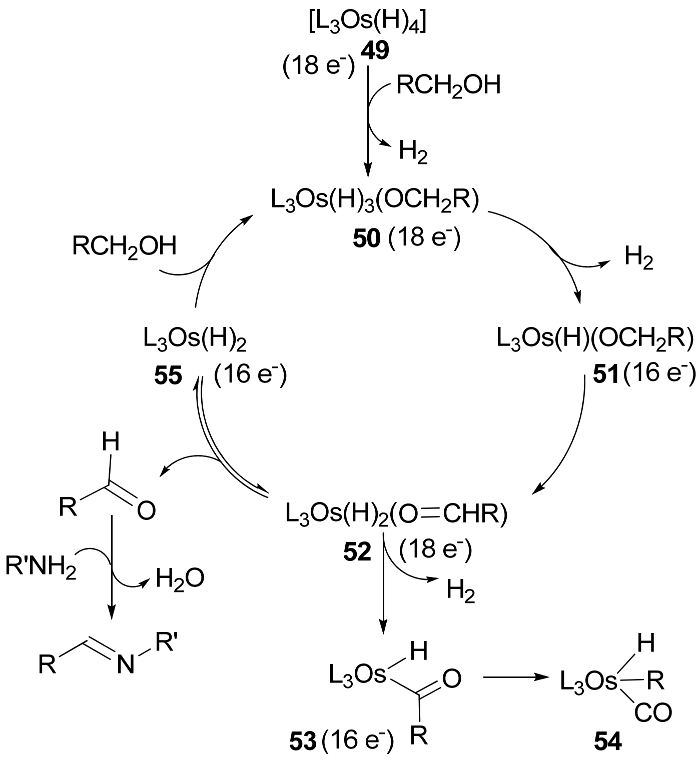
Scheme 25. Os-catalyzed dehydrogenative coupling of primary alcohols

Following Milstein's report on the ruthenium catalyzed synthesis of imines from alcohols and amines under clean release of hydrogen, Esteruelas *et al.* reported a polyhydride osmium complex **49** bearing a pincer-type POP ligand that, in a similar fashion, allowed access to imines (Scheme 26).[138]



Scheme 26. Imine synthesis by a polyhydride Os catalyst

A plausible mechanism is shown in Scheme 27. The catalytically active complex is accessible from the catalyst precursor **49** by protonolysis which leads to an osmium trihydrido alkoxo complex **50** and H_2 as entrance into the catalytic cycle. The saturated complex **50** loses an equivalent of H_2 giving the 16 electron complex **51**. Via β-hydrogen activation the alkoxy group is converted to the carbonyl species in complex **52**. Loss of the aldehyde product molecule – which reacts further with a primary amine to form the imine and water – again generates an unsaturated 16 electron osmium dihydride complex **55** which adds an alcoholic substrate molecule to turn the catalytic cycle over. This mechanistic proposition is bolstered to some extent by the isolation of complex **53** with R = Ph. This complex converts to the carbonyl complex **54** which is inactive and turns off the catalytic cycle. Furthermore, assuming an equilibrium between dihydride **55** and the aldehyde complex **52**, which is shifted towards **52** with increasing aldehyde concentration, rather fast catalyst deactivation via the exit to **53** and **54** can be explained as the alcohol conversion progresses. Strong bases lead to better catalytic performance by facilitating the imine formation and thereby preventing the decarbonylation of the aldehyde.



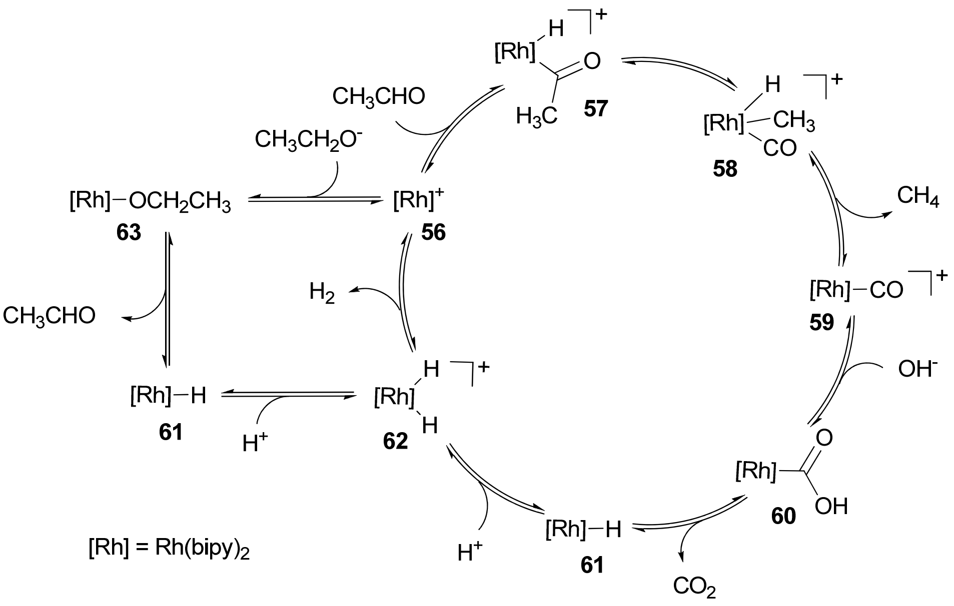
Scheme 27. Mechanistic hypothesis for the Os-catalyzed imine synthesis

This catalytic system allowed for the formation of aromatic as well as aliphatic imines in high yields, the latter being more challenging to synthesize. An advantage of this over Milstein's catalytic system relies on its shorter reaction time while the requirement of osmium as rather toxic and expensive metal is a drawback.

In late 1980s, Cole-Hamilton *et al.* reported the first hydrogen evolution from ethanol catalyzed by a rhodium complex in a thermal homogeneous process.[139] Using [Rh(Cl)(bipy)$_2$] as the catalyst and in presence of sodium hydroxide, decomposition of ethanol (containing 5% of water) was effected with TOFs up to 100 h^{-1} generating hydrogen, methane and carbon dioxide gases (Eq. 28).[140]

$$\text{Eq. 28} \qquad CH_3CH_2OH + H_2O \rightleftharpoons CH_4 + CO_2 + 2\,H_2$$

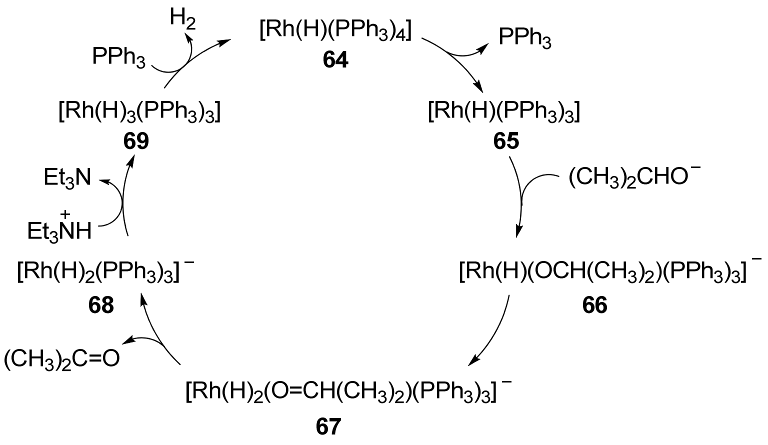
A mechanistic proposal is shown in Scheme 28. The interesting point of the catalytic cycle is the formation of a [Rh(CO)]$^+$ species (**59**) via complex **58** in a decarbonylation reaction of a metal bound acyl group (**57**). In presence of strong alkaline base, rapid nucleophilic attack of the hydroxide group leads to the formation of [Rh(CO$_2$H)] (**60**) which decarboxylates to the hydride [Rh(H)] (**61**). The high basicity of **61** allows the protonation generating the [Rh(H)$_2$]$^+$ (**62**) species in spite of the alkaline environment. The species **62** loses H$_2$ as final step in the Rh-catalyzed water-gas sift reaction H$_2$O + CO → H$_2$ + CO$_2$. However, this catalytic system was not very efficient in the dehydrogenation of methanol.



Scheme 28. Proposed catalytic cycle for the Rh-catalyzed decomposition of ethanol

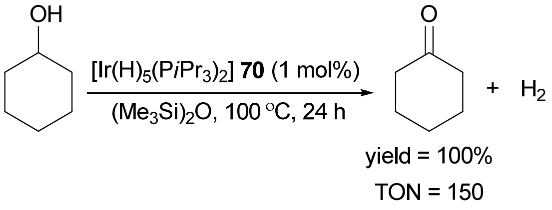
The same group reported also a process where secondary alcohols namely, 2-propanol and 2,3-butanol were dehydrogenated using a Rh(I)-catalyst producing hydrogen gas and the corresponding carbonyl compounds.[141]

Rhodium(I) catalyzed thermal dehydrogenation of 2-propanol was reported by Saito *et al.*[142] The simple rhodium hydrido complex $[Rh(H)(PPh_3)_4]$ (**64**) in presence of excess triphenylphosphine and triethylamine as additives, dehydrogenated 2-propanol generating equimolecular amounts of hydrogen and acetone. The proposed catalytic cycle is depicted in Scheme 29. In presence of triethylamine, the alkoxide ion of the corresponding alcohol is generated. From that, the alkoxide complex **66** is formed via complex **65,** which is obtained by dissociation of one equivalent of Ph_3P. Subsequent β-hydride elimination afforded the acetone complex **67**, that after liberating acetone formed the Rh(I)-dihydride complex **68**. Subsequent proton transfer to the metal centre from $[Et_3NH]^+$ gives the trihydride **69**. In the presence of triphenylphosphine, this complex loses one equivalent of molecular hydrogen and the catalytic cycle is closed with the regeneration of **64**.



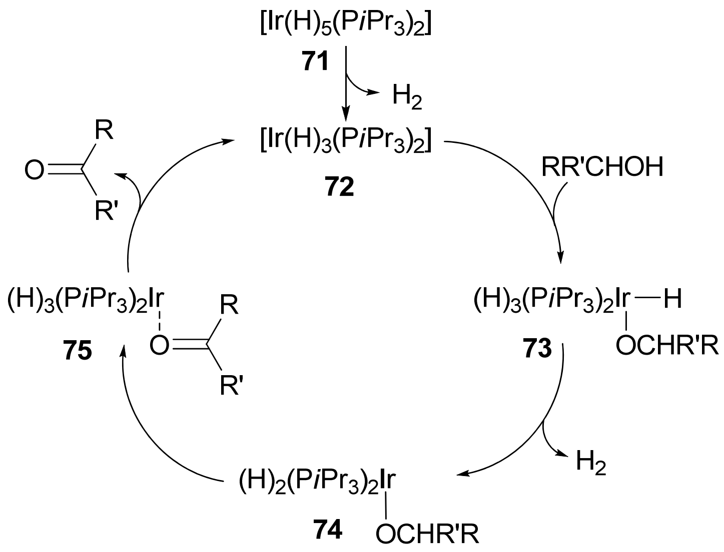
Scheme 29. Plausible catalytic pathway for the Rh-catalyzed dehydrogenation of 2-propanol

In 1987, Lu *et al.* discovered that Crabtree's iridium pentahydride complex $[Ir(H)_5(PiPr_3)_2]$ (**70**) can be used for the dehydrogenative oxidation of secondary alcohols in absence of any hydrogen or hydride ion acceptor.[143] A range of secondary alcohols both cyclic and acyclic were dehydrogenated to produce the corresponding ketone in moderate to high yield and TONs up to 150 were reached. The reactions were performed in hexamethylsiloxane as solvent at a temperature of about 100 °C (Scheme 30).[144]



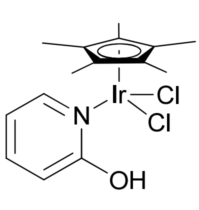
Scheme 30. Dehydrogenative oxidation of cyclohexanol catalyzed by a polyhydride Ir-complex

In the polyhydride complexes involved in the catalytic process, a dynamic equilibrium between classical dihydrides H-[M]-H and η^2-dihydrogen complexes [M]-(H_2) was proposed that leads to continuous hydrogen evolution. The proposed mechanism for this transformation is shown in Scheme 31. Initial reductive H_2 loss from the 18 valence electron configured pentahydride with iridium (**71**) in the oxidation state +5 generates the 16 electron Ir(III) complex $[Ir(H)_3(PiPr_3)_2]$ (**72**) with a free coordination site. This allows the addition of an alcohol molecule whereby the catalytic cycle is triggered. Subsequent loss of another H_2 molecule is followed by β-hydrogen activation of the metal bound O-CHR_2 group and formation of the carbonyl function in the coordination sphere of the iridium centre. The loss of the product molecule regenerates the Ir(III) catalyst **72** and turns the catalytic cycle over.



Scheme 31. Proposed mechanism for the Ir-catalyzed dehydrogenation of alcohol

Based on the concept of ”ligand-promoted dehydrogenation”, Fujita and Yamaguchi *et al.* has developed Ir(Cp*) derived complexes **76** – **79** with iridium in the oxidation state +3 that are able to oxidize primary and secondary alcohols and liberate molecular hydrogen (Figure 7).



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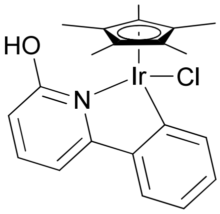

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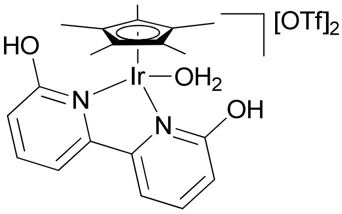

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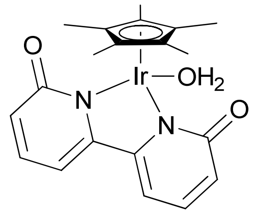
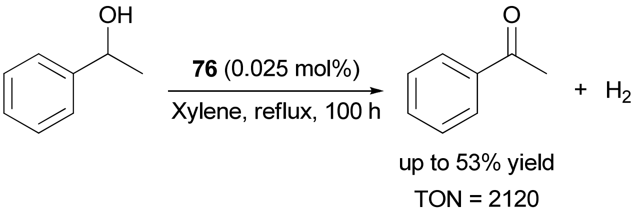


79

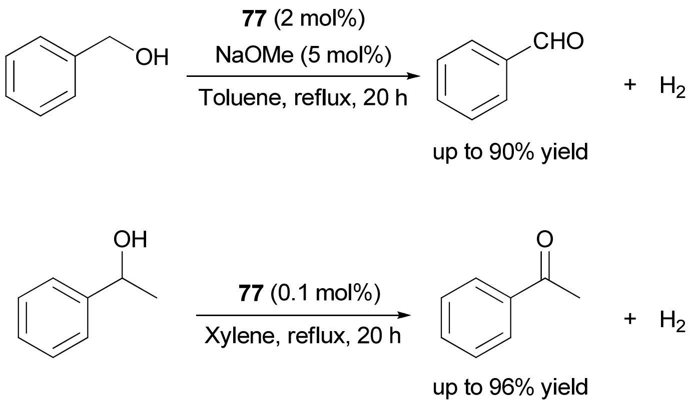
Figure 7. Ir(III) complexes used in the ligand-promoted dehydrogenation of alcohol

Complex **76** can dehydrogenate aromatic, aliphatic, and cyclic secondary alcohols in refluxing toluene in absence of any additive. The highest TON of 2120 was obtained when the reaction was performed in refluxing xylene (approx. 140 °C) in presence of 0.025% of catalyst **76** (Scheme 32) and needed extended reaction times (100 h).[145]



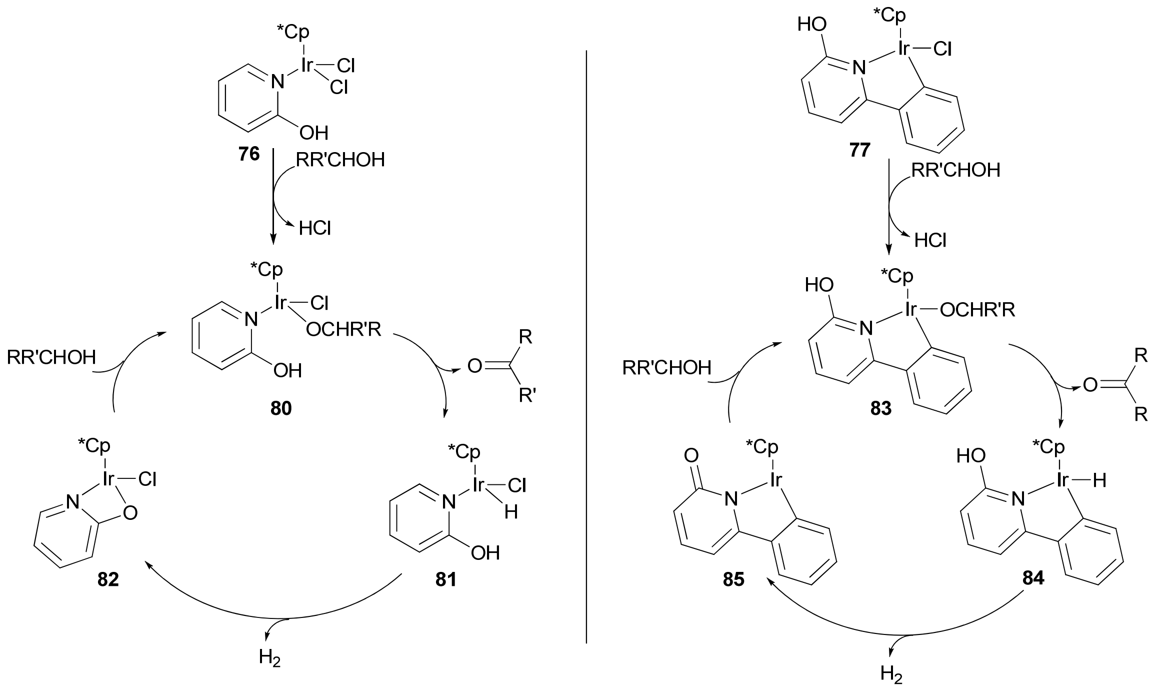
Scheme 32. Dehydrogenation of secondary alcohol catalyzed by complex **76**

Complex **76** was not efficient for the dehydrogenation of primary alcohols. But the Ir(Cp*) complex **77** with a C,N-chelating ligand is able to oxidize primary alcohols in moderate to good yields in the presence of bases such as Na(OMe) and Na(HCO_3). The oxidation of the aromatic and aliphatic secondary alcohols was achieved with excellent yields under neutral reaction conditions and relatively low catalyst loadings (0.1 mol%) (Scheme 33).[146]



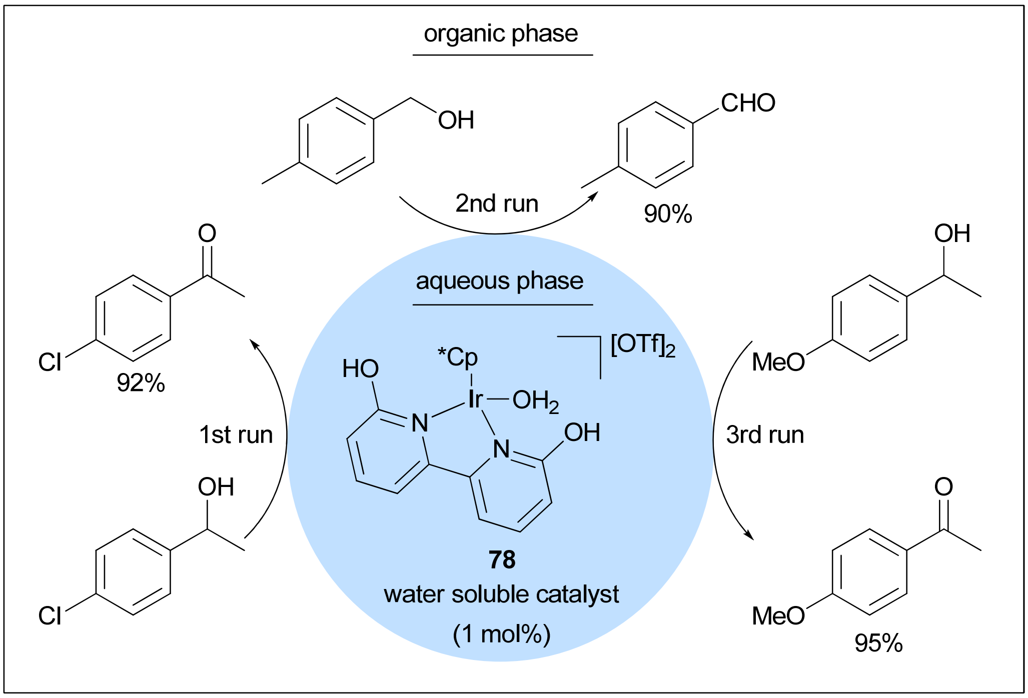
Scheme 33. Dehydrogenation of alcohols catalyzed by complex **77**

In the saturated 18 valence electron Ir(III) complexes **76** and **77** the ligands play a cooperative role as shown in the proposed mechanism for this dehydrogenative oxidation of alcohols (Scheme 34). In the first step a chloride ligand is substituted by an alkoxy group when **76** or **77** were treated with the corresponding alcohol. In the next step, β-hydride elimination occurs in the resulting iridium alkoxy complexes **80** and **83**, which generates iridium-hydride species **81** and **84** respectively and carbonyl compounds as products. Intramolecular protonolysis of **81** and **84** with hydroxyl groups on the ligand (cooperative metal-ligand effect) generates one equivalent of molecular hydrogen. Finally, the resulting iridium oxypyridyl complex **82** containing a four-member N,C,O-metallaheterocycle or the iridium pyridonate complex **85** react with alcohol molecules to give back the alkoxy iridium complexes **80** and **83** respectively and another catalytic cycle is started.



Scheme 34. Proposed catalytic cycle for the oxidation of alcohols catalyzed by **76** and **77**

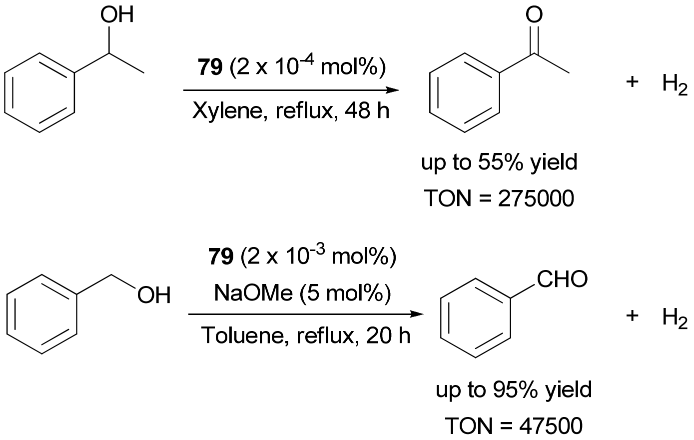
A further step forward towards a more efficient catalytic system working under environmentally friendly conditions was achieved when the same group introduced the dicationic iridium(III) complex **78** bearing a 2,2-bis(hydroxy)bipyridine ligand.[147] This complex performed the dehydrogenative oxidation of secondary and primary alcohols in good to excellent yields with TONs up to 2550 in aqueous media. The advantage of this water soluble catalyst system is that the aldehydes or ketones can be extracted into an organic solvent which allows separating the products from the catalyst by simple phase separation. This procedure also allows recycling the catalyst and it was shown that the iridium complex could be used eight times without significant loss in catalytic activity (Scheme 35).



Scheme 35. Schematic presentation of reusability of the water soluble catalyst **78**

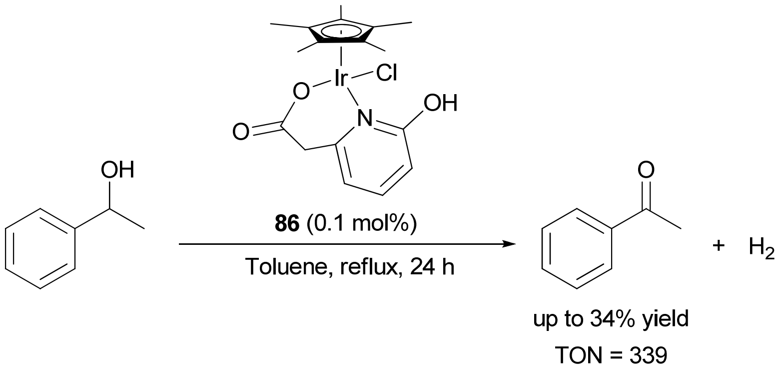
The efficiency of this catalytic system with complex **78** was demonstrated with the transformation of various primary and secondary alcohols.

The neutral iridium complex **79** with a dianionic bipyridonate ligand is related to **78** and is obtained by double deprotonation of the hydroxyl groups. The neutral complex **79** achieved the oxidation of secondary alcohols under mild reaction conditions (at 36 °C).[148] At elevated temperatures, in refluxing *p*-xylene (138 °C), the dehydrogenation of 1-phenylethanol proceeded with high efficiency and TONs up to 275000 was reached (Scheme 36). Benzyl alcohol afforded benzaldehyde in refluxing toluene (111 °C) and released hydrogen gas with TONs up to 47500 (Scheme 36).



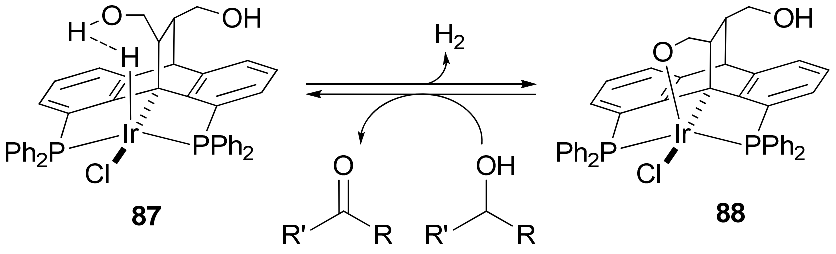
Scheme 36. Dehydrogenative oxidation of alcohols using catalyst **79**

In parallel to this work, Rauchfuss *et al.* reported dehydrogenative oxidation of 1-phenylethanol under liberation of molecular hydrogen utilizing the related complex [Ir(Cl)(Cp*)(Hcmhp)] (**86**) as catalyst.[149] In comparison to Fujitas catalysts, **85** showed moderate dehydrogenating activity (TONs up to 339) (Scheme 37).



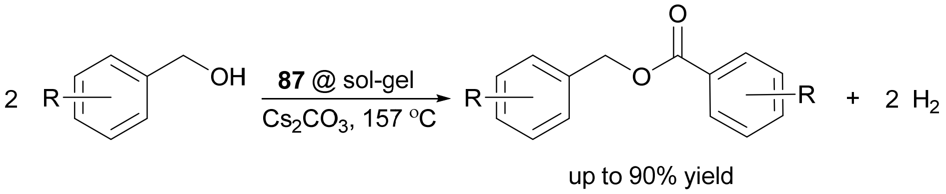
Scheme 37. Cp*-Ir(III) catalyzed dehydrogenation of a secondary alcohol

Another example of ligand assisted acceptorless dehydrogenation of alcohols was reported by Gelman *et al.*[150] The iridium pincer complex **87** showed catalytic activity for the transformation of a variety of primary and secondary alcohols into the corresponding aldehydes and ketones, respectively, and TONs up to 3600 were reached. The suggested key-steps in the reaction mechanism with this complex are presented in Scheme 38. Again, metal-ligand cooperativity is proposed. In complex **87**, the protic hydroxyl group interacts with the hydrido ligand and facilitates the release of one H_2 molecule. The resulting cyclic iridium alkoxy complex **88** reacts subsequently with the alcohol substrate to regenerate **87** and one equivalent of product. This mechanistic proposal is bolstered by the isolation of complex **88** which was also structurally characterized with X-ray diffraction methods.



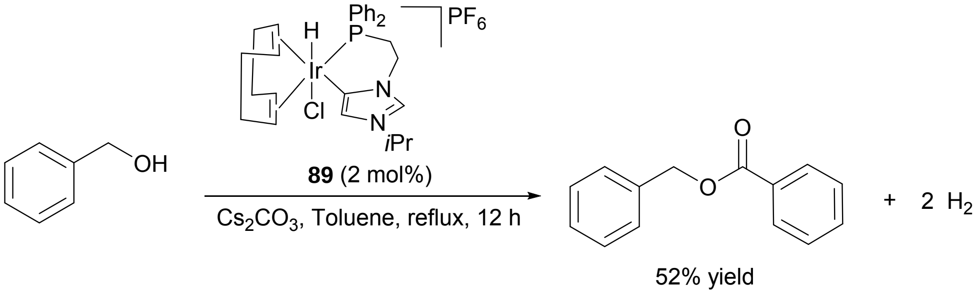
Scheme 38. Ligand promoted dehydrogenative oxidation of alcohol catalyzed by complex **87**

Catalyst **87** is air-sensitive which limits its application. Furthermore, it cannot be easily recycled. In order to circumvent these drawbacks, Gelman *et al.* incorporated the iridium catalyst **87** in a sol-gel matrix and thereby obtained a heterogenized catalytic system.[151] Although the immobilized catalyst needed higher reaction temperatures and higher catalyst loadings when compared to the iridium complex in homogeneous phase, the entrapment of the complex in the sol-gel afforded a recyclable catalyst that was capable of running five consecutive cycles without considerable loss in catalytic activity. This catalytic system cleanly converts secondary alcohols to the corresponding ketones. However, in the dehydrogenation of primary alcohols, RCH_2OH, a Tishchenko-type reaction was observed and the carboxylic esters were obtained as the major product (Scheme 39). This finding indicates that aldehydes, RCH=O, as intermediates react with non-reacted starting material to the corresponding hemi-acetals, $RCH(OH)(OCH_2R)$. These are then significantly more rapidly dehydrogenated than the alcohols used as starting materials.



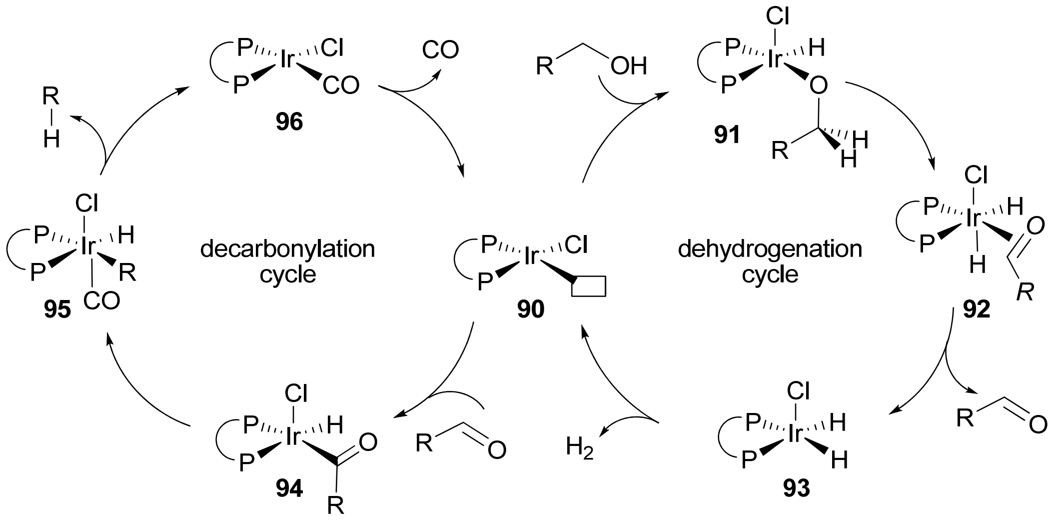
Scheme 39. Dehydrogenative coupling of alcohol using the immobilized catalyst **87**

In a recent study aimed at transfer hydrogenation of ketones and enones, Zhang *et al.* discovered the dehydrogenating properties of a cationic "abnormal" *N*-heterocyclic carbene iridium complex **89**.[152] This iridium complex was able to dehydrogenate benzyl alcohol to benzyl benzoate in 52% yield under the release of two molecules of hydrogen (Scheme 40).



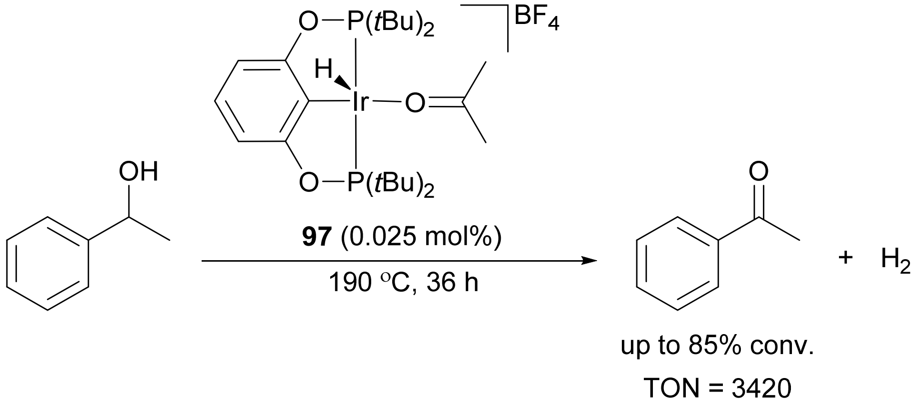
Scheme 40. Use of a carbene-Ir complex in dehydrogenative coupling of alcohol

Madsen *et al.* reported the dehydrogenative decarbonylation of primary alcohols to hydrocarbons liberating syngas as the further product. For example, 2-naphthyl alcohol was converted to naphthalene using $[Ir(coe)_2Cl]_2$ as the catalyst and *rac*-BINAP as ligand. A mixture of carbon monoxide and hydrogen was produced in absence of any scavenger.[153] In a plausible mechanism (Scheme 41), two consecutive catalytic cycles operating in parallel were proposed. The first one consists of a catalytic alcohol dehydrogenation yielding an aldehyde via a classical β-hydrogen activation of a primary alkoxy substrate coordinated to an iridium centre (**91**). This reaction leads to an iridium dihydride complex **93** from which H_2 is lost. The resulting highly unsaturated 14 valence electron configured iridium complex **90** oxidatively adds an aldehyde molecule via a C-H activation reaction and triggers the second decarbonylation cycle (Scheme 41). Besides the high reaction temperature, the major drawback of this reaction is the contamination of the hydrogen with carbon monoxide which makes the gas unusable in a fuel cell.



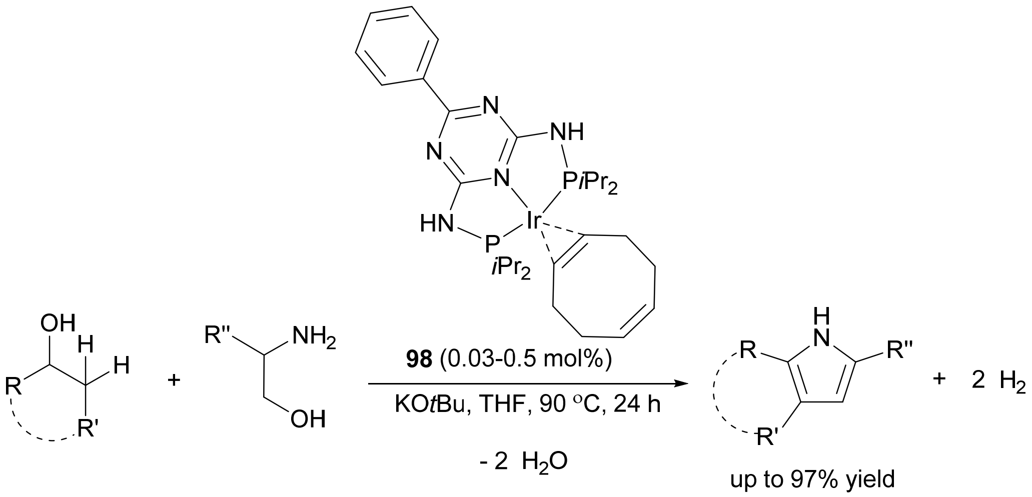
Scheme 41. Postulated catalytic cycle for the dehydrogenative decarbonylation of alcohol

An iridium pincer complex **97** bearing a bis(phosphinite)benzene ligand has been successfully applied in the dehydrogenation of secondary alcohols. Dehydrogenative oxidation of 1-phenylethanol afforded acetophenone with TONs up to 3420 under liberation of molecular hydrogen (Scheme 42).[154]



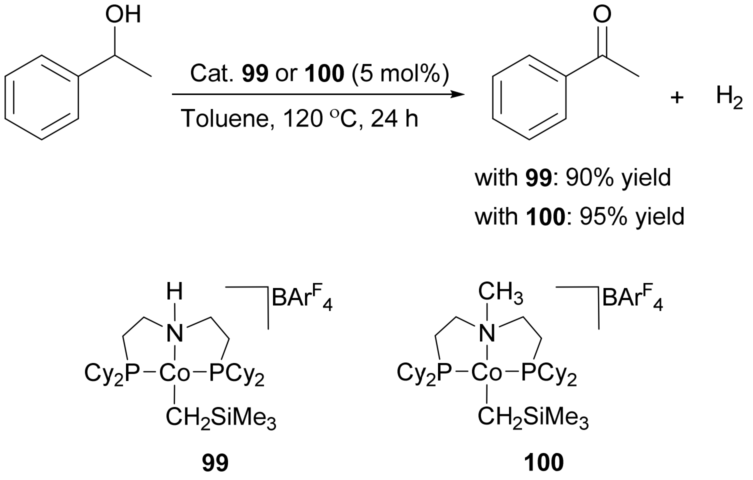
Scheme 42. Oxidation of alcohol catalyzed by the pincer Ir-complex **97**

In early 2013, Kempe *et al.* communicated a remarkable iridium catalyzed new synthesis of pyrroles from secondary alcohols and amino alcohols which proceeds under H_2 production.[155] In this reaction, the secondary alcohol and the amino alcohol were dehydrated and eliminated two equivalents of hydrogen molecules. Air and moisture stability of the iridium complex **98** and its high functional group tolerance combined with the fact that it offers highly substituted and bicyclic pyrroles makes this method an excellent choice for the synthesis of such heterocycles with very high atom economy.



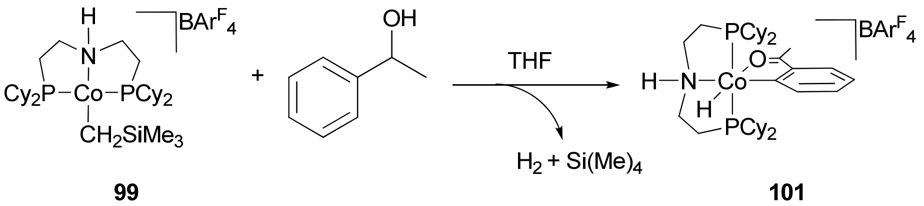
Scheme 43. Synthesis of pyrroles using Ir-catalyst **98**

Activity of cobalt(II) pincer complexes in the dehydrogenation of alcohols was reported by Hanson *et al.*[156] Co(II) complexes **99** and **100** ligated with aliphatic PNP pincer ligands converted 1-phenylethanol to acetophenone in high yields (Scheme 44). Comparable reactivity of both the complexes showed the little importance of the *N*-methyl substituent on the PNP ligand.



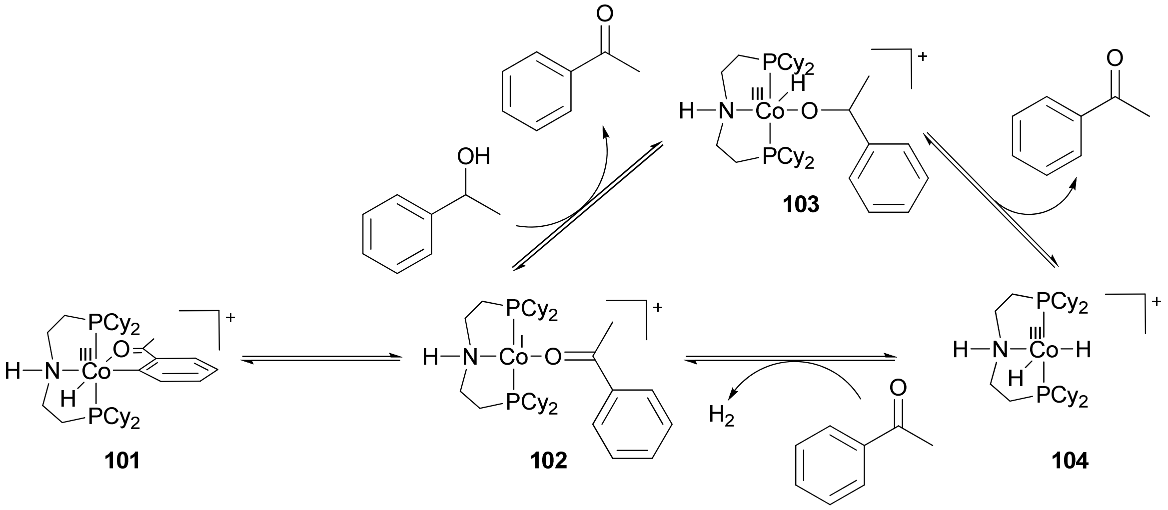
Scheme 44. Dehydrogenative oxidation of alcohol using Co(II) catalysts

A Co(III) aryl hydride complex **101** was isolated when the alcohol was reacted with complex **99** (Scheme 45). Deuterium labeling experiments identified cleavage of the α-C–H bond to be involved in this reaction.



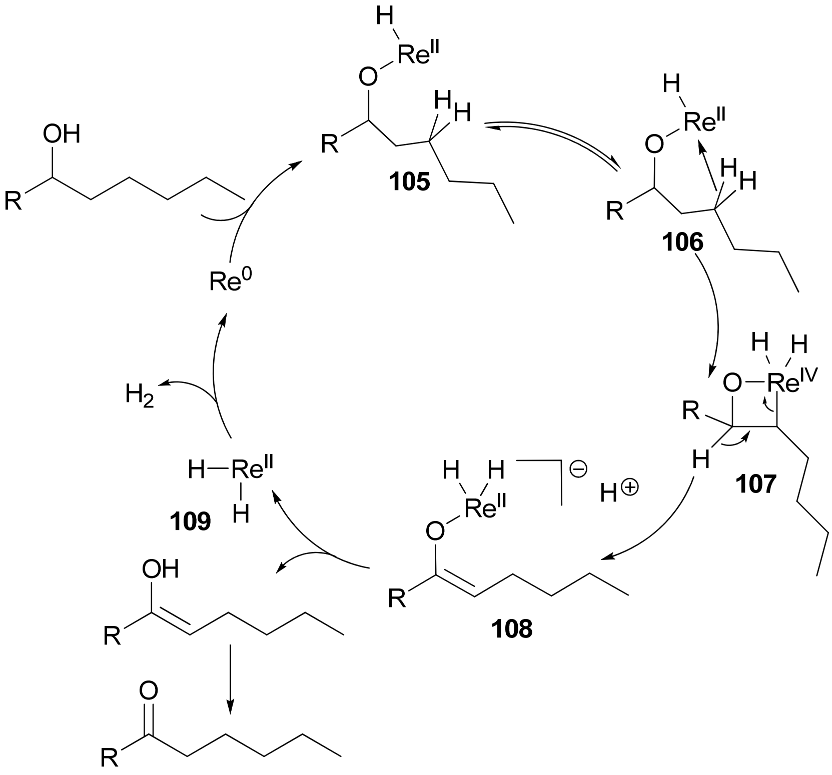
Scheme 45. Synthesis of Co(III) complex **101**

Complex **101** was found to have similar catalytic activity as compared to its parent complex **99** and hence, **101** was proposed to be the resting state of the catalyst in the mechanistic hypothesis presented in Scheme 46. Starting from **101** reductive elimination generates the cobalt(I) complex **102** which now can undergo a ligand exchange with another molecule of alcohol followed by an oxidative addition to give the cobalt(III) alkoxide complex **103**. The dihydride complex **104** was formed by β-hydride elimination of acetophenone. Removal of molecular hydrogen from **104** regenerated the Co(I) complex **102**. Metal ligand bifunctional catalysis is thus, operative in this dehydrogenative oxidation reaction.



Scheme 46. Proposed mechanism for Co-catalyzed dehydrogenative oxidation of alcohol

By the end of 2013, Abu-Omar *et al.* reported his findings on acceptorless dehydrogenation of alcohols using unsupported rhenium nanocrystalline particles (Re/NPs) as the catalyst.[157] When NH_4ReO_4 was refluxed at 180 °C in alcohol, Re/NPs (2 nm) were formed that oxidized an alcohol liberating molecular hydrogen. This catalyst system showed excellent activity in the oxidation of a variety of secondary alcohols to the corresponding ketones (up to 100% conversion) with a very good selectivity (up to 99%). Primary alcohols, with the exception of benzyl alcohol (55% benzaldehyde formation) showed poor conversion in this method for dehydrogenative oxidation. The kinetic isotope effect was determined (inverse KIE = 0.38) and indicates that a distinctive γ–CH activation is involved in this mechanism (Scheme 47).



Scheme 47. Catalytic cycle for the oxidation of secondary alcohol catalyzed with Re(0) nanoparticles

It is proposed that the alcohol oxidatively adds to the Re/NPs represented as Re(0) in Scheme 47, and the resulting alkoxy Re(II) species **105** after *γ*-C–H activation affords the Re(IV) metallacycle **107**. After ring opening and proton release, the α,β-unsaturated alkoxy Re(II) compound (**108**) is generated. The Re-O bond in this intermediate is cleaved by protonolysis and the α,β-unsaturated alcohol which isomerizes to the ketone is eliminated. The Re(II) dihydride (**109**) is formed which undergoes reductive elimination of one equivalent of hydrogen whereby Re(0) is regenerated and the catalytic cycle turns over.

3.2.3 Photochemical dehydrogenation of alcohols

Mononuclear complexes

The principle of microscopic reversibility dictates that any complex that is active for hydrogenation of a carbonyl compound should in principle also be active for the dehydrogenation of an alcohol. For that reason, well-known hydrogenation catalysts were investigated for the dehydrogenation of alcohols. Decarbonylation of the oxidized product has to be expected as an undesired side reaction, because many of the classical coordinatively unsaturated complexes involved in thermal hydrogenation/dehydrogenation reactions catalyse this follow-up reaction as well. In order to make the dehydrogenations irreversible, the reactions were performed under radiation with light. Sugi[158] and Smith *et al.*[159] discovered that the efficiency of the photolytic hydrogen generation is enhanced with Wilkinsons catalyst $[RhCl(PPh_3)_3]$ (in the presence of an excess of PPh_3 or $Ph_3P{=}O$). The authors observed that the catalyst was more efficient under aerobic conditions, required an induction period, and the catalyst performance was strongly dependent on the photon energy. The role of oxygen in the reaction remains speculative, but it was proposed that de-coordinated PPh_3 becomes oxidized to $Ph_3P{=}O$ which is a weak binding ligand and hence higher concentrations of unsaturated active Rh complexes are achieved. With the phosphite complex $[RhCl(P(OPh)_3)_3]$, TONs of 6410 h^{-1} for the dehydrogenation of 2-propanol were attained under radiation with UV light at room temperature. Light with longer wavelengths ($\lambda > 400$ nm) did not promote the reaction. The role of the photons is unclear but likely are involved in the photoextrusion of H_2 from the intermediate Rh(III) hydride complex $[RhCl(H)_2(PPh_3)_2L]$ (L = substrate). Vaska-type complexes like $[RhX(PR_3)_2(CO)]$ have also been employed as photocatalysts in the dehydrogenation of 2-propanol.[160] The efficiency of the reaction reached a maximum with $PR_3 = PEt_3$ and X = I achieving TOFs of 1114 h^{-1} at 84 °C. Importantly, the generation of hydrogen was best when the irradiation wave lengths (340 - 420 nm) coincided with that required for the removal of CO from the coordination sphere of the metal. This observation strongly supports a 14 e^- $[RhX(PR_3)_2]$ fragment as the active catalytic species.

Table 2. Active mononuclear complexes for the hydrogen production from secondary and primary alcohols under photolytic conditions

Catalyst	Alcohol	Product	Additives	λ_{exc} (nm)	T (°C)	TOF (h^{-1})	TON (H_2)	Ref
$[RhCl(PPh_3)_3]$	2-propanol	acetone	-	< 300	21	-	5370	159
$[RhCl(P(OPh)_3)_3]$	2-propanol	acetone	-	< 300	21	-	6410	159
$[RhCl(CO)_2]_2$	2-propanol	acetone	-	< 300	21		2980	159
$[RhBr(PEt_3)_2(CO)]$	2-propanol	acetone	-	340-420	84	750	-	160
$[RhI(PEt_3)_2(CO)]$	2-propanol	acetone	-	340-420	84	1114	-	160
$[RhBr(PMe_3)_2(CO)]$	2-propanol	acetone	-	340-420	84	810	-	160
$[RhH(P\textit{i}Pr_3)_3]$	EtOH	H_2/ CH_4	-	-	150	0.9	-	162

$[\mathrm{RhH}(\mathrm{P}i\mathrm{Pr}_3)_3]$	EtOH	H_2/ CH_4/ CO	-	>400	150	6.2	-	162
$[\mathrm{RuH}_2(\mathrm{N}_2)(\mathrm{PPh}_3)_3]$	EtOH	H_2/ CH_4/ CO	-	>400	150	14.5	-	162
$[\mathrm{RuH}_2(\mathrm{N}_2)(\mathrm{PPh}_3)_3]$	EtOH	H_2/ CH_4/ CO_2	NaOH	>400	150	210	-	161
$[\mathrm{RuH}_2(\mathrm{PPh}_3)_4]$	EtOH	H_2/ CH_4/ CO_2	NaOH	>400	150	138	-	161
$[\mathrm{RhH}(\mathrm{P}i\mathrm{Pr}_3)_3]$	EtOH	H_2/ CH_4/ CO_2	NaOH	>400	150	23	-	162
$[\mathrm{Rh(bipy)}_2]\mathrm{Cl}^a$	EtOH	H_2/ CH_4/ CO_2	NaOH	>400	120	95	-	161

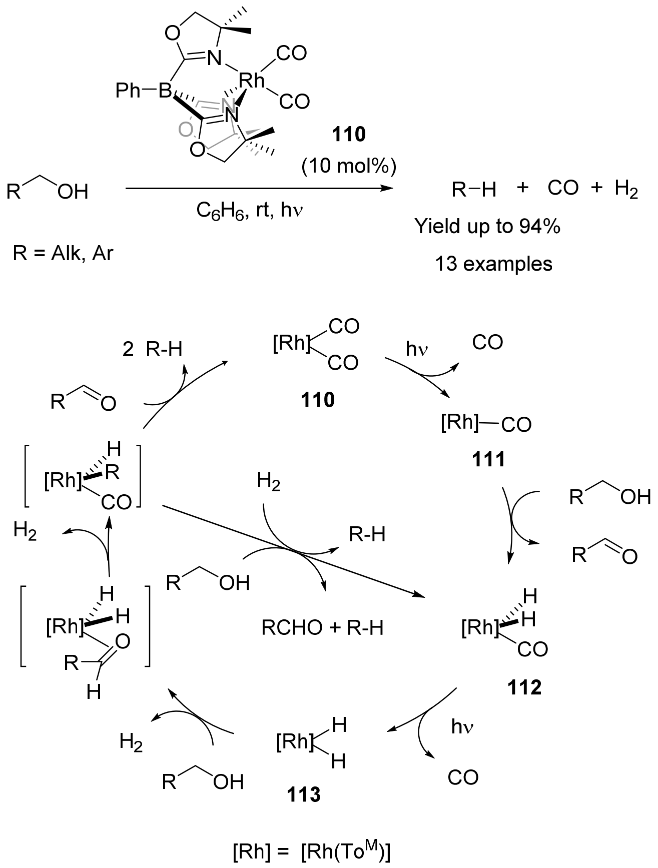
[a]Detected traces of ethanal and condensation products

The photochemical dehydrogenation of primary alcohols like ethanol can be catalyzed by classical hydrogenation catalysts such as $[\mathrm{RhCl}(\mathrm{PPh}_3)_3]$, $[\mathrm{RhH}(\mathrm{P}i\mathrm{Pr}_3)_3]$, $[\mathrm{RhH}(\mathrm{P}i\mathrm{Pr}_3)_3]$, $[\mathrm{RhCl(bipy)}_2]$, $[\mathrm{RuH}_2(\mathrm{N}_2)(\mathrm{PPh}_3)_3]$ and $[\mathrm{RuH}_2(\mathrm{PPh}_3)_4]$.[161] Under photochemical conditions, EtOH was catalytically dehydrogenated to give H_2, CH_4, and CO. If the poisonous CO, which is formed in a catalyzed decarbonylation reaction of aldehydes as intermediates, can be removed efficiently from the product mixture (by water gas shift reaction, see Eq. 24), the overall decomposition of alcohols proceeds according to Eq. 29 leading to hydrocarbons and hydrogen as energetic materials and CO_2.

Eq. 29 $RCH_2OH + H_2O \longrightarrow RH + CO_2 + 2\ H_2$

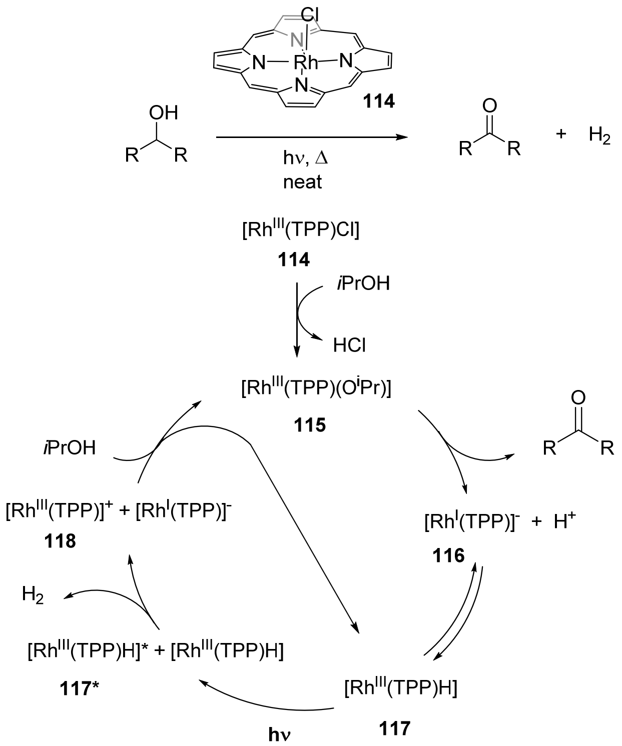
Capture of CO can be achieved by the addition of hydroxide ions as base whereby CO is continuously removed from the metal centre as CO_2. This reaction involves the addition of OH^- to coordinated CO promoting the release of CO_2 and the formation of a metal hydride. Indeed, Cole-Hamilton *et al.* reported the improved hydrogen release from a wide range of primary and secondary alcoholic substrates with rates up to 1000 h^{-1} when the metal complex $[\mathrm{RuH}_2(\mathrm{N}_2)(\mathrm{PPh}_3)_3]$ was combined with a base to give a catalytic system that operated under photochemical and thermal conditions (150 °C).[139162]

Sadow *et al.* showed that a photocatalytic deoxygenation of alcohols could be accomplished through a tandem dehydrogenation/decarbonylation process without sacrificial reagents promoted by the complex $[\mathrm{Rh(To^M)(CO)}_2]$ (**110**) [$\mathrm{To^M}$ = tris(4,4-isopropyl-2-oxazolinyl)phenylborate]. A wide scope of primary alcohols was efficiently converted into alkanes, CO, and H_2.[163] Although many mechanistic details remain speculative, the authors demonstrated that a) CO dissociation from the complexes $[\mathrm{Rh(To^M)(CO)}_2]$ (**110**) and $[\mathrm{Rh(To^M)H_2(CO)}]$ (**112**) is required to allow alcohol dehydrogenation, b) alcohols are more reactive than aldehydes towards $[\mathrm{Rh(To^M)(CO)}]$ (**111**), and c) $[\mathrm{Rh(To^M)H_2}]$ (**113**) formation and catalytic turnover is limited by a competition between CO and substrate for coordination sites at the metal. These observations are in agreement with the proposed mechanistic cycle showed in Scheme 48.



Scheme 48. Photocatalytic dehydrogenation of primary alcohols to alkanes and a proposed mechanism mediated by hydrido rhodium species

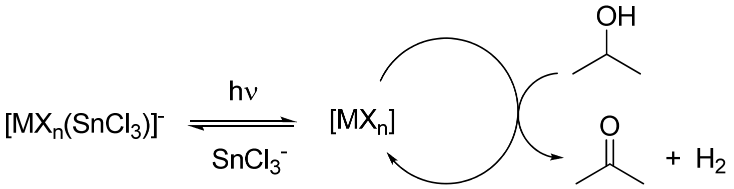
Metal porphyrins have been also used as photocatalyst in alcohol dehydrogenation. Ogoshi *et al.* reported in 1977 that hydrogen gas was evolved by heating a solution containing an hydridoporphyrin rhodium complex [Rh(OEP)H] (OEP = octaethylporphyrin, **L12** in Figure 4). Wayland *et al.* reported two years later that the hydrogen release rate is significantly enhanced under photochemical conditions[164] [165]Based on these findings, Saito *et al.* developed a catalytic process where the tetraphenyl porphyrin rhodium(III) complex $[Rh^{III}(TPP)Cl]$ (**114**) promoted the dehydrogenation of secondary alcohols. Neat 2-propanol[166]or cyclohexanol[167] were dehydrogenated to the corresponding ketones at reflux temperatures and radiation with visible light ($\lambda > 360$ nm) and long irradiation times. TOFs of 7 h^{-1} and TONs of 3430 were reached. The speculative photocatalytic cycle proposed by Saito *et al.* is shown in Scheme 49. The trivalent species $[Rh^{III}(TPP)]^+$ (**118**) reacts with 2-propanol to give acetone, $[Rh^{I}(TPP)]^-$ (**116**) and two proton equivalents. This dehydrogenative oxidation of the alcohol is not dependent on the radiation process. The complex $[Rh^{I}(TPP)]^-$ (**116**) is then protonated to the complex $[Rh^{III}(TPP)H]$ (**117**). Kinetic studies indicated that the reaction between a (π–π*)-photoexcited **117*** and a ground-state molecule of [Rh^{III}(TPP)H] results in the formation of H_2. The species [Rh^{III}(TPP)]$^+$ (**118**) and [Rh^I(TPP)]$^-$ (**116**) are obtained as products in a disproportion reaction. These intermediates activate a 2-propanol molecule and regenerate [Rh^{III}(TPP)H] (**117**) and [Rh^{III}(TPP)(O*i*Pr] (**115**) whereby the catalytic cycle is closed.



Scheme 49. Mechanism for the photocatalytic dehydrogenation of 2-propanol with Rh porphyrin complexes [Rh^{III}(TPP)X]

Binuclear complexes

Initial studies by Saito[168] have shown that homogeneous catalytic systems based on rhodium-tin complexes dehydrogenate secondary alcohols although with low catalyst efficiencies. A mixture of $RhCl_3$, $SnCl_2$, and LiCl dehydrogenated 2-propanol using UV light (254 nm) under reflux conditions achieving rates of TOF 6 h^{-1}($\Phi > 1$). In a following communication the same authors reported their investigations on the influence of the catalyst composition, temperature, and wave-length of radiation on the efficiency of the reaction. A TOF of 88 h^{-1} was attained and the quantum efficiency at 254 nm was estimated to be 2.2 at 82 °C. In order to rationalize quantum yields > 1, a mechanism was proposed in which irradiation into a M(dp)→Sn(p*) transition induces photolytic cleavage of the Rh-Sn bond and generates the coordinatively unsaturated active catalyst which is proposed to dehydrogenate 2-propanol thermally for several turnovers before it is trapped by ligand recombination with $SnCl_3^-$. The re-coordination of the tin ligand is assumed to be a fast process and no catalytic activity is observed when the irradiation source is switched off (Scheme 50).[169]

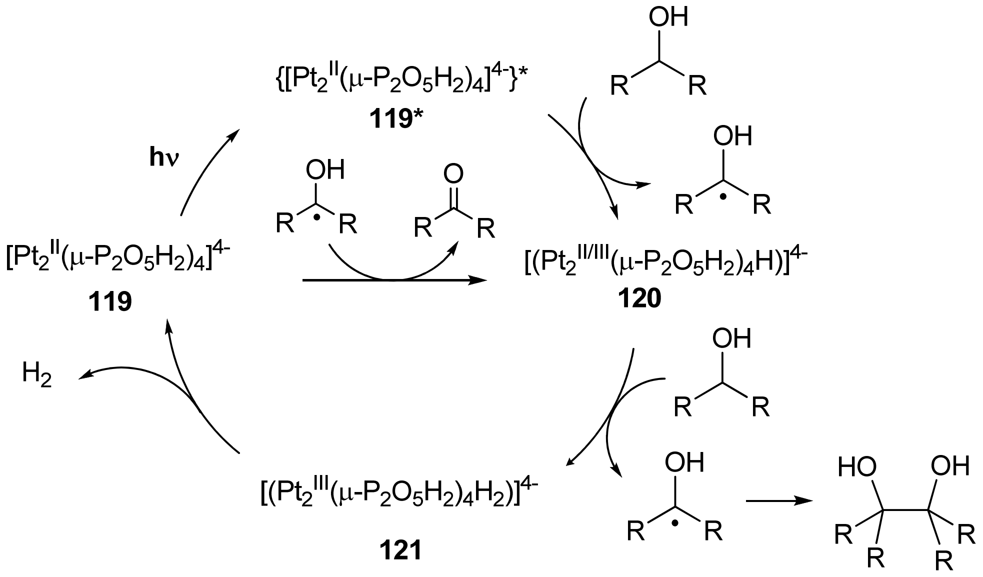


Scheme 50. Proposed mechanism of the catalytic cycle for 2-propanol dehydrogenation with Sn(II)-coordinated metal complexes. (X = Cl^-, $SnCl_3^-$)

A quantum yield of 12 for the same reaction was obtained with a Sn(II)-Ir(III) bimetallic complex, where the active catalyst was suggested to be either *trans*-$Ir^{III}Cl_2(SnCl_3)_4^{3-}$ or $Ir^{III}H(SnCl_3)_5^{3-}$.[170] Photocatalytic dehydrogenation activities of bimetallic Ir^{III}-Sn^{II} complexes formed *in situ* from $IrCl_3/SnCl_2/LiCl$ mixtures were obtained for methanol decomposition to molecular hydrogen and methoxyethane in an equimolecular ratio (TOF 1.1 h^{-1}). Addition of aqueous HCl enhanced the photocatalytic reaction rates up to 2.9 h^{-1}. Thermo- and photocatalytic dehydrogenation of 2-propanol was subsequently studied with a catalyst formed by simply mixing $RuCl_3$ with $SnCl_2$ in HCl aq. Spectroscopic studies indicated the formation of $[Ru(SnCl_3)_6]^{4-}$ and $[RuCl(SnCl_3)_5]^{4-}$ and the latter as the catalytically active species. As postulated for other M-Sn based catalysts, the dehydrogenation reaction of alcohols is mediated by unsaturated species formed by $SnCl_3^-$ dissociation upon irradiation and hydrido Ru intermediates may play an important role in the dehydrogenation.[171]

Alcohol dehydrogenation accompanied by H_2 evolution may also be accomplished by homonuclear bimetallic late transition metal complexes. Methanol and 2-propanol are photocatalytically dehydrogenated upon irradiatation with *cis*-$[Rh_2(\mu\text{-}Cl_2)(dpm)_2(CO)_2]$ or $[Pd_2(\mu\text{-}Cl_2)(dpm)_2]$ as catalysts (dpm = bis(diphenylphosphino)methane).[172,173] For methanol dehydrogenation the reaction rate was greatly enhanced by adding 10% acetone from TOF = 2.2 h^{-1} to 130 h^{-1}. The Pd complex showed a slightly better performance (TOF = 156 h^{-1}). Analysis of the gas phase demonstrated the presence of H_2 and traces of CH_4, while analysis of the liquid phase indicated the formation of formaldehyde, dimethoxymethane, ethylene glycol, 2,3-dimethyl-2,3-butanediol, 2-propanol and 2-methyl-1,2-propanediol. This product spectrum points to condensation and hydrogen transfer processes. The product distribution is significantly dependent on type of catalyst employed. While Rh catalysts favour the formation of ethylene glycol and formaldehyde, Pd based complexes give formaldehyde and its dimethyl acetal as mayor products. The authors investigated the rate, product distribution and quantum efficiency dependence of the acetone concentration and wave length of the irradiation for the Rh-catalyzed reaction. Control experiments using only acetone and no transition metal catalyst showed low catalytic activity and a markedly different product ratio. It was assumed that direct excitation into the $n \rightarrow \pi^*$ transition of the acetone molecule ($\lambda < 312$ nm) initiated the reaction and generated a ketyl radical and ${}^{\bullet}CH_2OH$ from methanol. Subsequent reaction of the Rh catalyst with the organic radicals yields formaldehyde, acetone and a rhodium hydride intermediate.

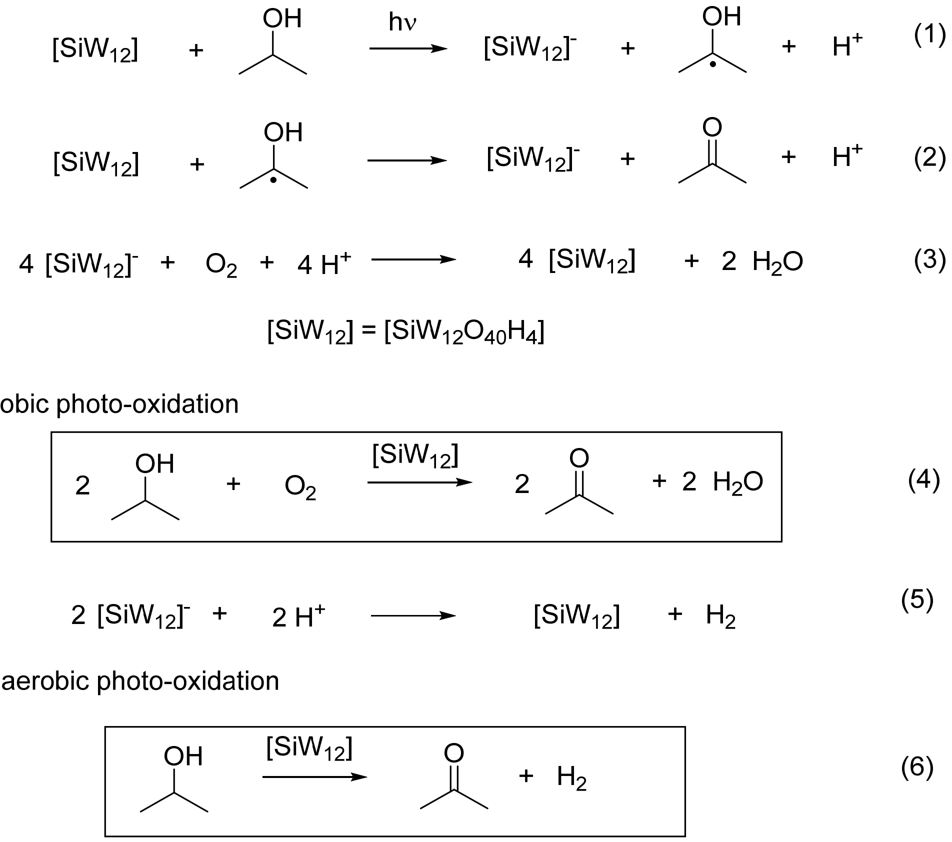
In 1977 Sperline *et al.*[174] reported an intense luminescence from a Pt(II) compound that was later identified as a dimer $[Pt_2(\mu\text{-}P_2O_5H_2)_4]^{4-}$ (Pt_2) (**119**) containing bridging P,P-bonded pyrophosphito ligands.[175,176] The electronic spectroscopy and photochemistry of these binuclear d_8-d_8 complexes have been studied extensively. The room temperature absorption spectrum of Pt_2 exhibits an intense band at 360 nm and a weak band at 450 nm that are assigned to the $d\sigma^*p\sigma$ singlet and triplet states (${}^1A_{1g}\rightarrow{}^1A_{2u}$ and ${}^1A_{1g}\rightarrow{}^3A_{2u}$).[174] Photophysical studies confirm that the properties of the photoactive excited state are a consequence of d_8-d_8 metal-metal interaction. An unusual feature of the complex is that aqueous solutions show an intense green emission at 514 nm. This long lived phosphorescence (τ = 9.8 μs) from a triplet excited state is accompanied by a shorter lived fluorescence (8 - 40 ps) at 407 nm. Triplet Pt_2^* is a one-electron reductant in aqueous solution and these reactions likely occur via an inner-sphere pathway at the vacant axial site of the Pt_2 dimer. Pt_2^* can also react as a free radical with an unpaired electron residing in a ds* orbital that is localized at an axial site. This free radical reactivity is manifested by atom-transfer reactions that occur without prior electron transfer. The ${}^3A_{2u}$ excited state of Pt_2^* abstracts hydrogen from a number of organic and organometallic substrates. In a pioneering report from Roundhill *el al.,* the binuclear species Pt_2 was established as the first photocatalytic system of platinum(II) complexes that converts isopropyl alcohol into acetone and hydrogen (TON of 400, TOF 133 h^{-1}).[177] From detailed studies of this system it was concluded that the first step is the abstraction of the α-hydrogen from 2-propanol by ${}^3Pt_2^*$ to form a divalent-trivalent dinuclear monohydride-bridged species $Pt^{II}(\mu\text{-}H)Pt^{III}$ (**120**) (detected by transient absorption spectroscopy).[178] Pinacol is found as by-product form the photoreaction and supports the suggestion of the formation of isopropyl radical intermediates. The mixed valence intermediate $Pt^{II}(\mu\text{-}H)Pt^{III}$ (**120**) abstracts a second H atom to form the trivalent dihydride, $Pt^{III}(\mu\text{-}H)_2Pt^{III}$ (**121**) in analogy to previously reported work on the thermal oxidation chemistry of Pt_2 complexes.[179,180] The complex $Pt^{III}(\mu\text{-}H)_2Pt^{III}$ thermally or photochemically reductively eliminates H_2 (Scheme 51). Gray *et al.* reported that Pt_2 is also a photochemical catalyst for the conversion of EtOH in hydrogen and acetaldehyde (TON = 33, TOF = 4.7 h^{-1}).[181] The proposed mechanism is shown in Scheme 51 and the reaction has been applied to numerous secondary alcohols as substrates using also iridium(I) dinuclear complexes as catalysts.[182]



Scheme 51. Mechanism for the photogeneration of H_2 from 2-propanol catalyzed by **119**

Polymetallic complexes

Polyoxometalates (POMs) are molecular oxides that contain early transition metals (usually M = Mo, W, less frequently V, Nb, Ta) in their highest oxidation states (d^0, d^1). These aggregates may contain a variety of heteroatoms like P, As, Si, Ge as few examples. Two general types of POM polyanions are distinguished in aqueous solutions: (i) isopolyanions $[M_nO_m]^{p-}$ and (ii) heteropolyanions (HPA) of general formula $X_sM_mO_n^{y-}$. The arrangement of twelve metal atoms (M = V, Nb, Ta, Mo, W) around one single heteroatom (X) form the basis of so-called Keggin structures where X/M = 1/12. The combination between two lacunary Keggin monomers $XW_9O_{34}^{z-}$ yields a dimer denominated Dawson POM, where X/M = 2/18. The assembly of two or several Keggin or Dawson fragments leads to the formation of more complex structures.[183] One of the most significant properties of POMs is their ability to participate in reversible electron transfer processes without decomposition or change in structure. POMs can be activated by near-UV photons in the presence of organic compounds (alcohols, acids) and give rise to blue species (HPB = *h*etero*p*oly*b*lue) with concomitant oxidation of organic compounds. In anaerobic solution, oxidation of alcohols to aldehydes or ketones by photoexcited POMs is accompanied by H_2 production. It was shown by several groups that it is crucial to use a cluster which can undergo multiple electron reductions in order to prevent cluster decomposition and allow catalytic turn-over.[184] Under aerobic conditions, the reduced HPBs are oxidized generating water as by-product.[185] Papaconstantinou *et al.* examined these processes in detail.[186] The low-energy electronic transitions are due to inter valence charge transfer (IVCT) bands within the lattice of polyoxymetallate. The HPBs are ESR active and at low temperatures give signals with hyperfine couplings indicative of localization of the unpaired spin on a single metal centre. The products obtained after two-electron reduction products are EPR-silent, indicating strong antiferromagnetic coupling of the unpaired spins within the lattice.[187] As the clusters typically contain oxidized d^0 metal centres, light absorption is mainly due to $(2n)O \rightarrow (d)M$ ligand-to-metal charge transfer bands in the region of 200 - 500 nm and as result the excited state possesses significant radical character on oxygen.[188,189] In general, two possible mechanisms are accepted depending if the reaction proceeds in the absence or presence of water molecules. Water molecules will attach to the cluster shell by hydrogen bonding. After photoexcitation of the M-O bonds, the bound H_2O molecules suffer from H-abstraction and form hydroxyl radicals, $OH^{\bullet}$ and protonated reduced M-OH species. In the absence of water, the alcoholic substrate is associated with the metal cluster and upon excitation H-atom abstraction from the alcohol is achieved directly by the oxo-radical in the cluster.[190,191,192] The extended degradation of 2-propanol to CO_2 and H_2 shows slow reaction kinetics which is 100 times slower than the conversion to acetone.[193] In Scheme 52 a proposed mechanism is shown for the photo-oxidation of 2-propanol by the heteropolyanion $[SiW_{12}O_{40}]^{4-}$ (SiW_{12}) (**122**) which under anaerobic conditions proceeds with formation of hydrogen. The reduction potentials for heteropolytungstates are sufficiently low in order to reduce water in acidic solution (pH < 6),[194] so reaction (3) can be replaced by reaction (5) and the overall reaction reads as: 2-propanol + hv → $Me_2CO + H_2$ (6). Darwent *et al.* demonstrated that the rate of H_2 production can be accelerated in the presence of a heterogeneous catalyst. The quantum yield for H_2 production from a solution of 0.5 M $MeOH$-H_2SO_4 (1:1) containing Pt (0.002 mol%) and SiW_{12} (0.02 mol%) was 0.1 mol Einstein^{-1} at 340 nm, which is suitable for conversions using solar energy. A system based solely in SiW_{12} absorbs light only below 360 nm and is not applicable. Other alcohols like propanol, ethanol and 2-propanol were tested and the highest relative rates were observed for the secondary alcohol. Recently Muradov *et al.* tested the potential of using polyoxometalates of tungsten for solar hydrogen production using alcohols as feedstock in a photocatalytic flat-bed reactor of small portable-pilot plant dimensions. A reaction mixture consisting of an aqueous solution of 2-propanol or sugar with isopolytungstates ($[W_{10}O_{32}]^{4-}$ or $[SiW_{12}O_{40}]^{4-}$) and colloidal Pt as photo-catalytic system was pumped through fused-silica tubes equipped with solar concentrators and exposed to sunlight. With this solar photoreactor a steady-state production of hydrogen gas of 180 mL h^{-1} was achieved for several days using a radiation reflux of 800-1000 W m^{-2}.[195]

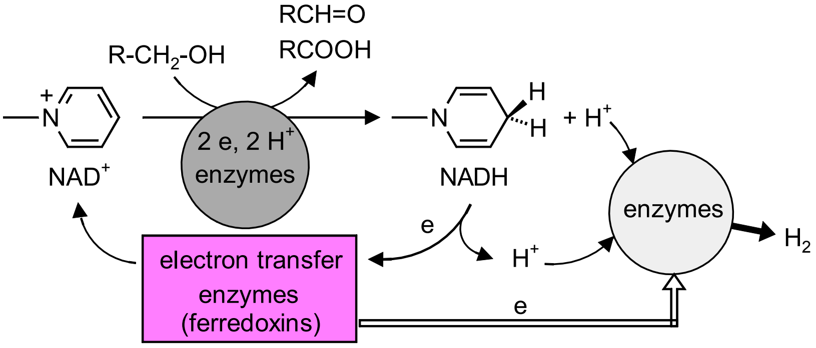


Scheme 52. Photo-dehydrogenation of 2-propanol under aerobic or anaerobic conditions using dodecawolframosilic acid

4. *Concluding remarks and outlook*

Over the last decades from the discovery that metal complexes can cleave off molecular hydrogen from alcohols, the dehydrogenation of these substances has been developed into a very active and focussed topic of research. Without question this research is driven by the desire to develop alternative methods to ensure mankind with a sufficient energy supply using rapidly renewable resources.

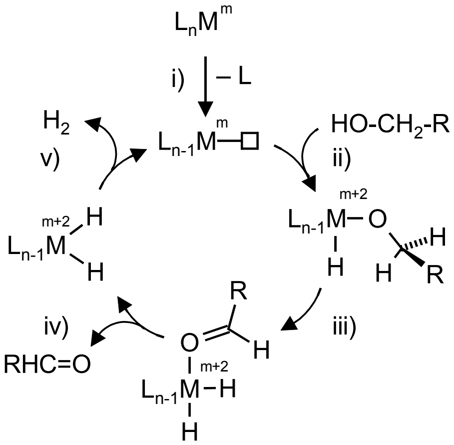
Biological organisms have developed over millions of years a rather complicated machinery by which alcohols are converted to carbonyl compounds (aldehydes, carboxylic acid derivatives) and hydrogen. Several enzymes are involved in this process as shown in a highly simplified sketch in Scheme 53. The conversion of alcohols is promoted by enzymes like alcohol dehydrogenase and aldehyde dehydrogenase. In this process, two protons and two electrons are involved which convert NAD$^+$ into its reduced form NADH and a proton equivalent. Electron transfer enzymes like ferredoxines reconvert NADH into NAD$^+$ and a second proton equivalent. These protons are reduced with the help of a third type of enzymes (hydrogenases or nitrogenases) using the electrons stored in the ferredoxines to dihydrogen.



Scheme 53. Schematic representation of the dehydrogenation of alcohols which requires various enzymes. Hydrogen is produced by reduction of protons with electrons stored in ferredoxins with the help of hydrogenases or nitrogenases.

With this approach nature achieves a spatially and timely resolved oxidation of alcohols and reduction of protons. This allows for a specific control over each reaction step and the implementation of repair mechanisms. These enzymatically catalyzed processes are highly efficient, especially the ones catalyzed by hydrogenases, and achieve turn over frequencies in seconds which are not reached by man-made catalysts within an hour.

The first investigations into artificial hydrogen-evolving processes with organometallic complexes were inspired by the mechanistic understanding which evolved from homogeneously catalyzed hydrogenation reactions. Indeed, many complexes which were successfully applied in hydrogenations like Rh(I) complexes (see Schemes 28 and 29 for examples) were investigated as dehydrogenation catalysts as well. Generally, it is assumed that these reactions proceed via classical steps which are very well established in organometallic chemistry and in Scheme 54 we show a simplified mechanism. In most cases, the metal complex [ML_n] which is used in the reaction needs to be activated by loss of a ligand L to generate an unsaturated complex [ML_{n-1}] which is the true catalyst (step i). The "free" coordination site, which is mostly occupied by a weakly bound solvent molecule, is indicated by a square. In the next step (ii) an alcohol molecule is bound to the metal centre for example via an oxidative addition. Subsequently, the α-CH bound in the coordinated substrate is activated by the metal centre, the C-H bond is broken and hydrogen is transferred to form a metal dihydride in step (iii). A molecule with a C=O double bond is released in step (iv). The loss of molecular hydrogen in step v) closes the catalytic cycle and regenerates the catalyst.

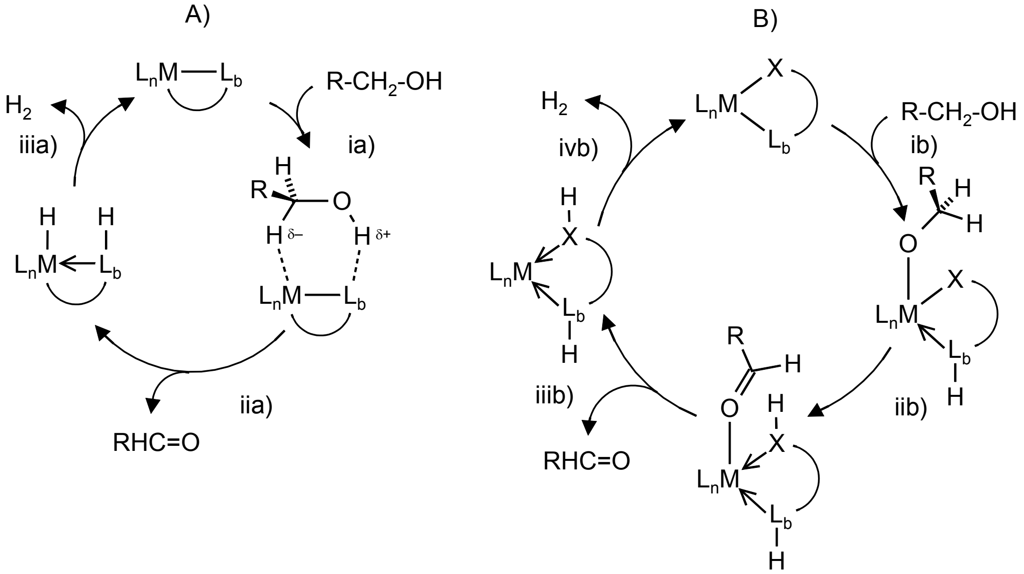


Scheme 54. Classical organometallic catalytic cycle which involves activation (i), oxidative addition (ii), β-hydrogen elimination (iii), product dissociation (iv), and reductive elimination (v).

With variations, the catalytic cycles shown in Schemes 27 – 31 correspond to this approach. Catalytic turn over frequencies and turn over numbers are rather low and at best a few thousands were reached so far with ruthenium complexes like the Robinson catalyst, $[Ru(OCOR_F)_2(CO)(PPh_3)_2]$. The rather low conversion rates are likely due to the fact, that either the oxidative addition or the reductive elimination requires rather high activation barriers.[196] Note, that the oxidation states of the metal centre change in course of the catalytic cycle which provokes significant structural changes of the metal complexes which are involved in the catalytic cycle. This makes an accurate design of the structure of the metal complex difficult. Sterically bulky ligands will favor the stability of the unsaturated metal complexes $[ML_n]$ but at the same time may lead to higher activation barriers for reaction steps within complexes with higher coordination numbers [c.f. steps (ii) and (iii)].

More recently, organometallic complexes were developed which benefit from metal ligand cooperation. Scheme 55 shows two simplified cycles which highlight the role of the cooperating ligand which directly and reversibly participates in the chemical transformation of the substrate molecules. Mostly the cooperating ligand is a chelating ligand (indicated by a bow "$\cap$") which is tightly wrapped around the metal centre and contains one or more functional sites. In cycle A) the ligand has a basic cite, L_b, and DFT computations suggest that the alcohol molecule adds with the protic OH group to the ligand and with the weakly "hydridic" α-CH bond to the metal centre [step (ia)]. In a more or less concerted reaction, hydrogen is transferred as "krypto"-hydrogen ($H^{\delta-}$,$H^{\delta+}$) to the metal complex and the dehydrogenated molecule is released [step (iia)]. In step (iiia), hydrogen is dissociated from the M-L_b bond in the complex and the catalytic cycle turns over. Anionic amide functions, NR_2, directly connected to the metal centre proved to be especially effective as basic cooperating ligand, L_b (see for example rodium(I) amides in Scheme 10, and ruthenium amides in Scheme 15). However, the good performance and broad applicability of Milstein-type catalysts like

[RuH(CO)(PNN)] (**25**) show that the basic site may reside in a remote position with respect to the metal centre.



Scheme 55. Two possible catalytic cycles with complexes that show metal-ligand cooperativity. Note that in cycle A, the metal centre does not change its oxidation state and the substrate molecule is bound in the second coordination sphere. In cycle B, the substrate binds to the metal centre and the α-CH-bond is cleaved by an active site X in the ligand. The arrows are meant to indicate that the quality of the M-L_b or M-X bond changes (from a covalent bond "–" between M and an anionic L_b or X ligand to a "coordinative" bond "→" between a L_bH or XH as neutral two electron donor ligand).

A slightly different approach is shown in Scheme 55B. Here the cooperating ligand contains two active sites, L_b and X, and both participate in the transformation of the substrate. In the first step the polar OH bond of the alcohol is added across the polar $M^{(\delta+)}$-$L_b^{(\delta-)}$ bond with the metal centre as Lewis-acid and the ligand as Lewis-base [step (ib)]. In the second step (iib), an active site X in the ligand which can be a weakly Lewis-acidic or basic or radicaloid site abstracts the α-CH hydrogen centre and performs the dehydrogenative oxidation of the alcohol to a carbonyl species which is released in (iiib). A thermal dehydrogenation of the ligand occurs in step (ivb) and closes the catalytic cycle. While the metal oxidation state does not change in cycle A, this cannot be ruled out in cycle B and has been demonstrated with the ruthenium complex [Ru(trop$_2$dad)] shown in Scheme 15. This complex carries a redox- and chemically non-innocent ligand and the metal oxidation state does change by two units within the catalytic cycle. The electronic character of the metal ligand bonds changes: in Scheme 55, a covalent, shared two-electron bond between the metal and an anionic ligand is given by "–" while a coordinative dative bond between the metal and a neutral ligand is indicated by arrows. Special cases are complexes with so called PNN and PNP pincer ligands (see

Schemes 13, 14). With these the highest activities were reported (up to 2670 h^{-1}). The role of the coordinated NH function, which is easily deprotonated to form an amide and a L_b active site, is clearly established. It is, however, suspicious that the highest activities are observed with pincer ligands which have ethylene bridges, $-CH_2-CH_2-$, in their backbone. It may very well be that these become reversibly dehydrogenated and hydrogenated whereby the mechanism switches from A to B. Catalytic systems which show metal ligand cooperativity show generally significantly higher activities than classical complexes. A principal advantage of this type of catalyst is that they do not need an activation step by ligand dissociation. Note that in catalysts following the steps shown in cycle A, the substrate molecule binds in the second coordination sphere which minimizes severe structural changes in the first coordination sphere of the catalytically active complex. This feature facilitates a catalyst design and indeed catalysts which show metal-ligand cooperativity can be directly synthesized and isolated. Because the binding of the substrate molecules in the second coordination sphere – frequently achieved through hydrogen bridges – is weaker than the direct binding of the substrate molecules to the metal centres in classical complexes, the activity of the catalyst is sensitive to steric effects. Too large substituents which reach into the binding site for the substrate molecule will lower the conversion rates by several orders of magnitude.

Which future developments can be foreseen? Catalysts which show metal-ligand cooperativity offer an enormous potential for future developments and are expected to provide significant improvements in the conversion of renewable alcohols into chemicals and hydrogen by finding the perfect electronic and steric match between a metal and its ligand. Numerous combinations including ligands which were specifically synthesized for metal-ligand cooperativity are possible. Likewise, the combination of fuels as listed in Table 1 offers much room for improvements. At present it seems that coupling reactions in which two “fuel” molecules are combined under the evolution of hydrogen proceed with higher efficiency than for every fuel alone. With these catalytic systems, new devices may be constructed like *o*rgano*m*etallic *f*uel *c*ells (OMFCs) in which no elemental hydrogen but electric current and protons are produced according to $H_2 \leftrightarrows 2\,H^+ + 2\,e^-$. It may be questioned whether these devices can contribute substantially to the production of energy but they may lead to the development of fine-chemicals from renewable sources with a minimum of waste (the only by-product is electric current). OMFCs powered by an alcohol may also find applications in small portable electronic devices and medicinal implants.

The photocatalytic conversion of alcohols and sugars into dehydrogenated oxidized products and hydrogen must find more attention in the future. Although the first experiments were carried out about four decades ago, there is relatively little progress. Most remarkable are photocatalytic conversions of alcohols which proceed under deoxygenation, that is the alcohols are directly converted to carbon monoxide, hydrocarbon, and hydrogen, $R\text{-}CH_2\text{-}OH \rightarrow RH + H_2 + CO$. The use of sunlight to achieve this process efficiently is a significant breakthrough for the development of a H_2 economy.

As the development of highly efficient fermentation processes advances, which provides ethanol from vegetable waste, the demand for catalysts to convert ethanol with a minimum of loss of energy will increase. The benchmark to date is the dehydrogenative coupling of two ethanol molecules to ethylacetate and two equivalents of hydrogen which proceeds with a TOF of 15000 h^{-1} using metal complexes with cooperative pincer ligands. The conversion of methanol as an almost ideal liquid fuel is much more challenging. But recent progress gives reasons to hope that new catalyst and catalytic systems will be found which show even higher activity and especially longevity.

The hydrogen production from alcohols with organometallic complexes has come some way and made good progress with respect to efficiency. But there remains a very long way to be walked before catalytic systems are developed which can halfway compete with biological systems. Organometallic chemistry can provide a strong impetus especially with respect to a better mechanistic understanding of key-steps in the dehydrogenation of alcohols and related molecules from renewable biomass. The ultimate goal will and must be to develop organometallic complexes which contain earth abundant, little-toxic, and cheap metal centres and ligands which are prepared with components that do not consume more energy than the device can deliver during its life-cycle. In that respect, phosphorus containing ligands which are frequently encountered are almost prohibitive given that the production of elemental phosphorus from phosphate rock requires 46000 kJ. Here again the creativity of chemists is challenged in order to find alternatives.

Acknowledgments: The own work cited in this paper was supported by the ETH of Zurich and the Swiss National Foundation (SNF). Also, the dedication of the master, PhD students, and post-doctoral fellows to their work which helped expand our knowledge a little bit of how to transform alcohols catalytically with transition metal complexes is gratefully acknowledged. Their names are listed in the cited publications.

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